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# HYDROGEOLOGIC EVALUATION OF A SUBSURFACE OIL SPILL AT THE METAL BANK OF AMERICA, INC. DISPOSAL SITE PHILADELPHIA, PENNSYLVANIA

# HYDROGEOLOGIC EVALUATION OF A SUBSURFACE OIL SPILL
at the
METAL BANK OF AMERICA INC. DISPOSAL SITE
PHILADELPHIA, PENNSYLVANIA

FINAL REPORT


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for

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United States Coast Guard
Marine Environmental Unit
USCG Base Gloucester
Gloucester, N.J.


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# SECTION 1

# INTRODUCTION

## 1.1 PROBLEM DEFINITION

During September 1977, Marine Environmental personnel of U.S. Coast Guard (USCG) Base, Gloucester conducted initial sampling and analysis of an oil seep discharging into the Delaware River from a riverfront property of Metal Bank of America, Inc. These samples of the seep were collected for PCB analysis by the U.S. Environmental Protection Agency (U.S. EPA) field laboratory in Annapolis, Maryland. Subsequent detailed studies conducted at the site included drilling, coring and sampling in the suspected spill area. As a result of the data collected, a scope of work for a detailed site investigation was prepared by the U.S. EPA and Pennsylvania Department of Environmental Resources (DER) geologists. Roy F. Weston (Weston) was selected to perform the study as detailed in this prepared work scope.

## 1.2 LOCATION

The Metal Bank of America, Inc. property involved in this study is an area of made land in the tidal Delaware River. It is located in the vicinity of Cottman Avenue, Philadelphia, (Figure 1.1), 1.2 miles seaward of Philadelphia Water Department's Torresdale water intakes. The site is presently being used for storage of scrap materials including transformer casings, condensers, paper insulation, fabricated sheet and bar metal and other unidentified materials.

## 1.3 PURPOSE

The scope of work performed under Contract No. DOT CG 03-7493, dated 9 March 1978 is contained in the 15 November 1977 proposal by Weston to Captain K. G. Wiman, USCG Base, Gloucester. Briefly summarized, the tasks of the contract were as follows: 1) sample existing well points and oil discharge areas, 2) conduct a hydrogeologic analysis of the site and 3) sample and analyze PCBs in site soils and ground water. These tasks were designed to provide detailed information on the following:

- Migration patterns of oils and PCBs within and surrounding the spill site.
- Potential migration patterns of oils and PCBs to the Delaware Estuary.

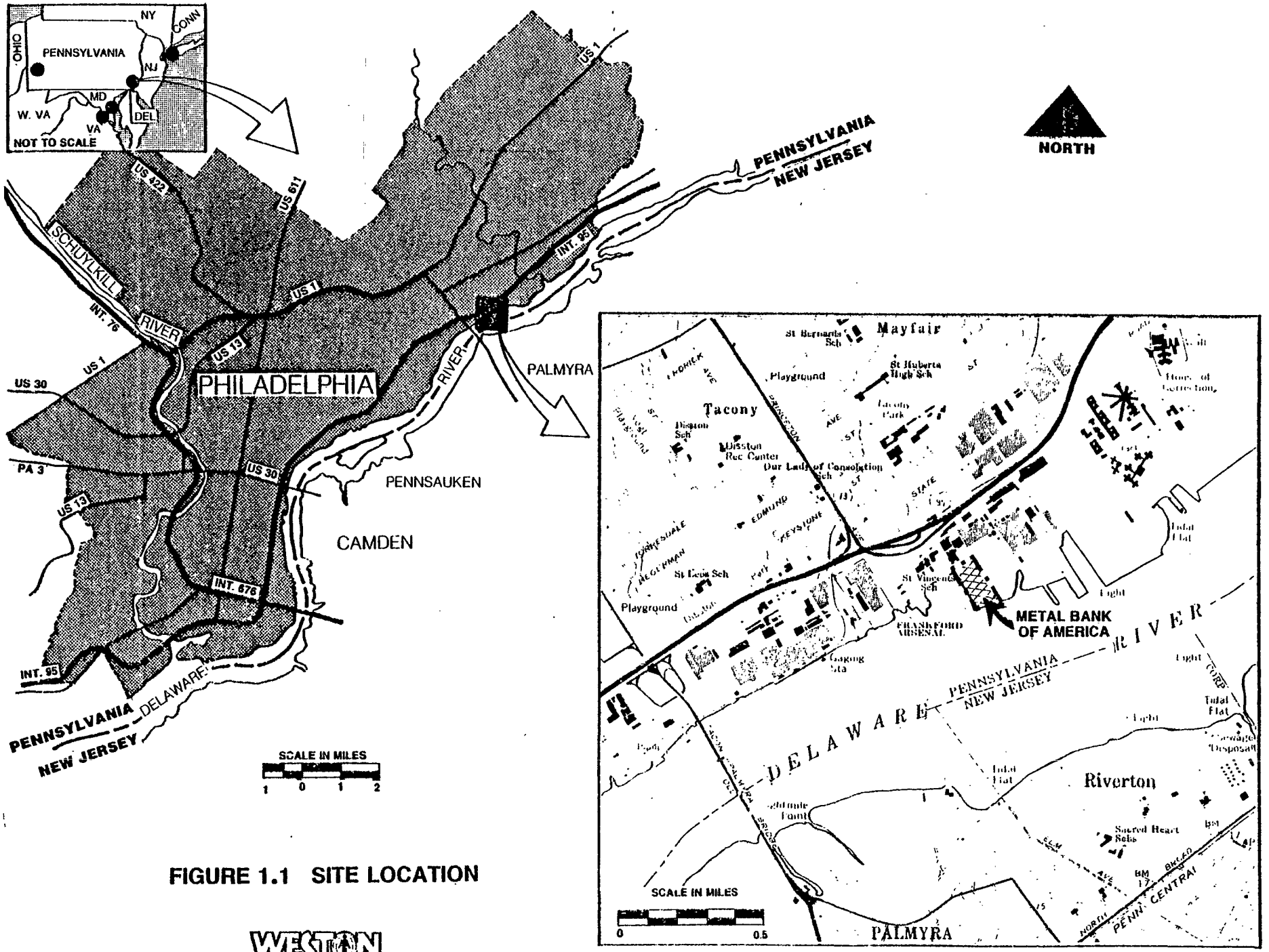


**FIGURE 1.1 SITE LOCATION**

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- Estimation of the volume of oils containing PCBs within the site area.
- Potential contamination of site biota by PCB uptake.
- Conceptual site cleanup procedures.

## 1.4 RESULTS OF PREVIOUS INVESTIGATIONS

As a result of the initial site investigations by the U.S. EPA cited above, the following site conditions were determined and reported to the Regional Response Team:

- The site consists of about 10 to 15 feet of artificial fill over a gently sloping, compact clay. The area of concern centers around a buried, 6,000-gallon tank (Figure 1.2) which was previously used for temporary storage of transformer oil containing PCBs. The oils were transported to the site in electrical transformers, which were reportedly disassembled on the site during the period 1968 to 1972.
- Surface materials in the area of the tank were oil-soaked. Ponded surface water on the site was noted to have oil sheens.
- The buried oil tank was found to be full of water with several inches of oily sludge in the bottom.
- Three driven observation points (wells) were installed by the U.S. EPA. These are indicated on Figure 1.2 as EPA-1, EPA-2 and EPA-4. Soil and liquid samples were collected from these wells and analyzed for PCB content.
- The intertidal zone on the perimeter of the property contained a zone of oil seepage estimated to be 70 feet long. A hand-dug hole in this area revealed approximately three inches of oil-contaminated soil. Oil which seeped into the hole was sampled by the U.S. EPA.
- Results of analyses of soils and liquids sampled at the site indicated that PCBs are present. Results of these analyses are included in Table 1.1. PCB concentrations ranged from undetectable in some soil samples to 1539 ppm in the oil floating on the ground water in observation point EPA-2.

TABLE 1.1

Results of PCB Analyses from Previous Investigations

| EPA LAB NUMBER | SAMPLING LOCATION | DATE COLLECTED | PCB CONCENTRATION * |
|---|---|---|---|
| 73-1357 | Metal Bank of America Site | 7/6/73 | 134.0 ppm |
| 73-1358 | Oil Slick in Delaware River | | 802.0 ppm |
| 77091401 | Oil/Water Collected in Intertidal | | 775 ppm |
| 77091402 | Zone Near Metal Bank | 9/12/77 | Not Run |
| 77091403 | Cottman Ave. Prop. | | Not Run |
| 77091404 | | | Not Run |
| 77091701 | Torresdale Water Treatment Plant (Raw) | | 0.26 ppb |
| 77091702 | Torresdale Water Treatment Plant (Combined Finished | | 0.055 ppb |
| 77092201 | Surface Sample by Observation Well EPA-1 | 9/21/77 | 14.6 ppm |
| 77092202 | EPA-1 2-4 ft Sediment | 9/21/77 | N.D. |
| 77092203 | EPA-1 4-6 ft. Sediment | 9/21/77 | 22.1 ppm |
| 77092204 | EPA-1 9 ft Sediment | 9/21/77 | 4.3 ppm |
| 77092205 | EPA-1 12-14 ft Sediment | 9/21/77 | Not Run |
| 77092206 | EPA-1 Oil on water table 9'8" | 9/21/77 | 1079.0 ppm |
| 77092207 | EPA-2 2-4 ft Sediment | 9/21/77 | 8.2 ppm |
| 77092208 | EPA-2 6-8 ft Sediment | 9/21/77 | N.D. |
| 77092209 | EPA-2 10-12 ft Sediment | 9/21/77 | 16.4 ppm |
| 77092210 | EPA-2 Oil on Water Table 10' | 9/21/77 | 1539.0 ppm |
| 77092211 | EPA-3 Abandoned Sample Point | 9/21/77 | Not Run |
| 77092212 | EPA-4 4-6 ft. Sediment | 9/21/77 | 5.8 ppm |
| 77092213 | Intertidal Area, Oil on Water, See Map | 9/21/77 | 1071.0 ppm |
| 77092214 | Mud Flats, Sediment, See Map | 9/21/77 | 619.0 ppm |
| 77092215 | EPA-4 10' Sediment | 9/21/77 | N.D. |
| 77092216 | EPA-4 16' Sediment | 9/21/77 | Not Run |
| 77092217 | EPA-4 Oil on Water Table 10'6" | 9/21/77 | N.D. |
| 77100503 | Bottom Sludge from Storage Tank | | 38.0 ppm |
| 77101305 | Oil Slick in Delaware River | 9/21/77 | 981.0 ppm |

N.D. - Not Detected

* PCB Concentrations reported as Arochlor 1260-
Analyses Performed by US EPA Laboratory,
Annapolis, Maryland

# SECTION 2

# METHODOLOGY

## 2.1 GENERAL SAMPLING PROCEDURES

Because of the possibility that PCBs might be found in the materials to be sampled, the following precautions were taken with sample containers and sampling procedures to avoid cross contamination:

- One-liter, brown, wide-mouth, glass, sample bottles were washed thoroughly with nanograde acetone, rinsed with distilled, double-deionized water and then baked two hours at 200°C. Teflon or aluminum-foil cap liners were similarly prepared. Bottles were opened immediately before sampling, then sealed and labelled immediately afterward. Samples were refrigerated for delivery to the laboratory and a chain of custody document accompanied each sample. A duplicate copy of the document remained in the Weston project control file.

- Sampling apparatus, including split-spoon samplers, drill rods, pumps, hoses, knives and any other equipment which had sample contact were washed between samples with nanograde acetone and rinsed with distilled, double deionized water. Drill augers and split-spoon samplers were washed with nanograde acetone and rinsed with distilled, double deionized water after completion of each well.

- Project personnel were provided rubber footwear, inhalers for organic vapors and gloves as safety equipment. Use of this equipment was recommended within a defined precaution area.

## 2.2 SPECIFIC SAMPLING PROCEDURES

### 2.2.1 Initial Surface Soil Sampling

#### 2.2.1.1 Location and Distribution

Initial surface soil sampling at the Metal Bank site was performed on 12 April 1978. Seven surface soil samples were collected in the intertidal area to independently evaluate the presence of PCBs in the oil seeps observed. Three other samples were collected on the site surface, away from any obvious source of contamination. The locations sampled, MBS-1 through MBS-10 (shown on Figure 1.2), were determined by pacing.

2.2.1.2 Sample Collection Procedures

These initial soil samples were collected with a hand pick and a PCB prepared sample bottle as grab samples from the near surface seepage face. The hand pick was washed with a brush and water and then thoroughly rinsed with nanograde acetone and distilled, double deionized water after each sample pit was dug.

The sample size was 25 or more grams of soil. Sequential sample numbers were recorded on the sample bottles and chain of custody sheets. Refrigerated samples were delivered to the laboratory for analysis. Analysis was conducted as described in Section 2.2.6 of this report.

2.2.1.3 Permeability Testing

Permeability of the site soils was measured by a "slug" test. Distilled, deionized water was used for this measurement to reduce the potential for additional contamination by standard drawdown test. Permeability was then calculated using the Ernst equation.[1]

2.2.2 Construction of Test Wells

2.2.2.1 Location and Distribution

Nineteen monitor well points were constructed by Weston to provide hydrologic, chemical and oil occurrence data at the site. The well points drilled under Weston's supervision are designated MB-B1 through MB-B19. The three monitor points installed by the U.S. EPA are designated EPA-1, EPA-2 and EPA-4. The locations of these wells are shown in Figure 1.2.

After construction, surface elevations and locations of the monitor well points were established by Weston surveyors. For the purposes of this study, a temporary benchmark was established on the site and monitor well elevations shown refer to this assigned datum.

2.2.2.2 Construction Details

The well points constructed under Weston supervision for this report were drilled using hollow stem augers. A split-spoon type sampler was used to obtain an undisturbed soil sample by the Standard Penetration Test procedure (ASTM D1586). These undisturbed samples are taken at

[1] Chow, V.T. ed 1964, Handbook of Applied Hydrology, McGraw Hill Book Company, New York

periodic intervals through the hole. After completion of the drilling, a well screen and pipe casing were installed through the hollow core of the augers. The well screen was located so that the fluid level at the time of completion was centered in the screened interval. This was done to allow for tidal fluctuations of the fluid surface within the well. The annular space surrounding the well screen was backfilled with clean gravel to assure hydraulic connection between the monitoring point and the aquifer. The remainder of the hole was then backfilled with site material. The wells were allowed to equilibrate for at least five days before sampling.

Well screens used in Weston wells MB-B1 through MB-B17 were commercially prepared 2.25-inch O.D. 12 slot PVC screen in three-foot bare lengths.

PVC well screens were chosen rather than metal screens for the following reasons:

- Interferance with gas chromatography analyses was found to be less of a problem with brittle PVC screens than with coated metallic screens.
- Non-equilibrium sampling procedures were used to insure that the sample quality accurately reflects the quality of fluid from the surrounding aquifer.

The bottom of the well point was capped and 1 1/2-inch I.D. Schedule 40 PVC riser pipe was installed with unglued, pressure-fitted slip joints. Casing stick-up above ground was between one and four feet.

Wells MB-B18 and MB-B19 were drilled to determine the presence and lithologic character of the deeper layers. For these wells, 1 1/2-inch Schedule 40 PVC pipe was field slotted for use as screens. The bottom eight feet of pipe in Well MB-B18 and the bottom 10 feet of casing in Well MB-B19 were slotted.

### 2.2.3 Hydrogeologic Monitoring

Fluid levels in the well points were measured on several occasions. The procedure used was to coat a steel tape with water-indicating paste and to lower the tape into the well below the fluid surface. The fluid level and oil thickness is then read off the tape. Between observations, the tape was washed as described in Section 2.1 above.

### 2.2.4 Water/Fluid Chemistry

Fluids from 17 Weston and one EPA observation wells were sampled for PCB analysis. The samples were obtained by non-equilibrium pumping.

With this technique, the wells are allowed to equilibrate prior to measuring and sampling. Before the samples were collected, the fluid level in the well was lowered by pumping about three times the volume of fluid in the well. This lowered water level forces flow into the well, which is collected by further pumping.

The pump used for this sampling was a new Guzzler brand hand bilge pump. The pump and tubing were rinsed with nanograde acetone and distilled, double deionized water between each sample. A one-liter sample was then collected from each well. Care was taken to insure that no air was trapped inside the bottle with the sample. Samples were refrigerated for delivery to the laboratory.

2.2.5 Biotic Sampling

On 25 May 1978, four plant samples from the Metal Bank property were collected by Weston for determination of PCB content. The primary objective of this reconnaissance survey was to determine if predominant plant species within the site contained PCBs. Since the site is a disposal area, it is almost devoid of vegetation. Each plant sample (about 50 grams/sample) was a composite of leaves or leaves and stems of a single species collected within an approximately 0.1 acre plot (Figure 2.1). All samples were placed in PCB prepared glass jars and immediately placed on ice packs. The samples were kept refrigerated until they were analyzed.

2.2.6 Analytical Laboratory Procedures

Analyses were conducted according to the methods outlined in Federal Register, Volume 38, No. 125, 29 June 1973, Part II: "Sediment Extraction Procedures for the S. E. Water Laboratory, EPA", Athens, Georgia, Method No. SP-8/71 (Appendix B). Specifications for the equipment used appears in Table 2.1.

Extraction procedures are included in the specified analytical methods. Florisil partitionings for soil extractions were optional, depending upon the cleanliness of the sample. The minimum detectable concentration of Arochlor 1016 in soil samples is 20 to 50 ppb. The minimum detectable concentrations in water samples is 50 ppt.

In this method, a calibration factor and peak area were used to calculate the amount of Arochlor 1016 injected. Actual retention time, with a 1.5 percent window, was used to identify the Arochlor peaks.

Differentiation of Arochlor 1016 and Arochlor 1242 is sometimes possible because the relative areas of the peaks of Arochlor 1016 are different from the relative areas of peaks of Arochlor 1242. Furthermore, Arochlor 1242 has two additional peaks with longer retention times than any of the Arochlor 1016 peaks. Details of analytical equipment used in these analyses is presented in Table 2.1.

Table 2.1

Details of Analytical Equipment Used for PCB Analysis

| | |
|---|---|
| Instrument: | Varian 3700 Automated Gas Chromatograph with a CDS.111 data system and a Model 8500 liquid sampler. |
| Column: | Glass, 2 meters x 2mm I.D. |
| Packing: | 1.95% SP-2401 (equivalent to QF-1) and 1.5% SP-2250 (equivalent to OV-17) on 100/120 mesh Supelcoport. |
| Injection Port Temperature: | 200°C |
| Column Temperature: | 200°C, isothermal |
| Detection: | $Ni^{63}$ pulse frequency, 300°C |
| Carrier Gas: | Nitrogen, 40 mls/min. |

| | |
|---|---|
| % recovery water samples | 90-95% |
| % recovery soils | 75-80% |

Standards & spiked samples extracted with samples.

See also Appendix B for more details

# SECTION 3

# DISCUSSION OF FINDINGS

## 3.1 SURFACE OBSERVATIONS

### 3.1.1 Physical Setting

During the course of the field work, oil was observed seeping into the Delaware River along the Metal Bank property. At high tide, the seeps were identified at areas "A" and "B" on Figure 1.2, where oil rose to the water surface as a series of drops. These two to four inch diameter drops spread out to a sheen when they broke the water's surface. On several occasions, the sheen was observed coalescing into a continuous oil slick which was driven down the river (seaward) by the wind and falling tide. On a rising tide, the seep at "B" (Figure 1.2) formed a similar slick extending up the river.

At low tide, the oil seep along the western side of the site was marked by a tar-like deposit in the intertidal zone. It extended almost continuously from the fence at the southwest corner of the Reischer Ford lot to sampling site MBS-3, a distance of about 125 feet ("A" on Figure 1.2). No tar-like deposit was observed between MBS-3 and the southwest corner of the site. The riprap material in the southwest corner was not heavily oil-stained, however, riprap material near sampling stations MBS-6 and MBS-7 ("B" on Figure 1.2) was heavily oil-stained where a small flow of oil was observed coming out of the rocks and running out into the river. Dark oil rapidly collected in pits dug for samples MBS-6 and MBS-7.

Stiff grey clay underlies the fill along the shoreline of the site. This clay is overconsolidated with respect to its thin overburden, and it is, therefore, felt to represent natural river bottom material. River bottom sediments in the cove west of the site consisted of 3 to 12 inches of extremely loose silt, clay and organic matter over a stiff, grey clay. Small, localized patches of oil spotting were observed. The thickness of the oil was sufficient only to cause a surface sheen in discrete, isolated spots. Oil was observed only on the sediment surface, and not at depth.

On the Metal Bank site, oil contamination of the surface materials was extensive. Oil sheens were observed on the surface of pools of standing water within the site.

Large mounds of paper from wire insulation wrappings were lying about the site (Figure 1.2). It is not known whether they represent a source of PCBs, since past PCB use has included fiber insulation material as well as transformer fluids and capacitor dielectric fluid.

### 3.1.2 Biotic Sampling

Four vegetation samples were collected from the site (Figure 2.1). The plant materials were leaves and stems collected within the first foot

above the ground surface. The PCB content of the four samples analyzed range from 2.6 to 4.2 ppm (Table 3.1). These concentrations are noteworthy because the background concentration of PCBs in plants is normally below limits of detection. These compounds do not naturally occur in the environment. The literature suggests not only that root uptake of chlorinated biphenyls occurs (dependent upon soil concentrations), but also that the lesser chlorinated biphenyls are translocated through the plant, volatilized from the soil and possibly redeposited on aboveground plant tissues to a greater extent than are the higher chlorinated compounds.

Of the four samples collected, the two samples collected closer to the transformer disassembly area contained higher concentrations than the two taken distant from this area (Figure 2.1 and Table 3.1). However, because of the small number of samples collected, and the narrow range of values observed, no spatial trend can be established.

As previously mentioned, the site is almost devoid of vegetation and, as such, has minimal value to local wildlife; the only observed animal life utilizing the site being several nesting killdeer and a feral cat. Rodents are expected to be a key component of the site animal life. The mud flat southwest of the site appears to be of minimal value to wildlife. No gastropods or other surface life were observed and a cursory screening of sediments yielded no benthic macroinvertebrates.

## 3.2 SUBSURFACE OBSERVATION

Two of the Weston test borings (MB-B18 and MB-B19) were designed to penetrate into the natural material below the site fill. One U.S. EPA well (No. EPA-4 on Figure 1.2) also penetrated the entire thickness of the fill. A stiff, grey clay was encountered in each of these borings. The elevations of the top of this clay stratum below the site and its lithologic similarity to the clay observed along the western shoreline of the stream in the cove west of the site, suggest that it is a continuous horizon.

The clay is interpreted to be natural riverbottom material. It is similar to colloidal clays which possess hydraulic conductivities on the order of $10^{-7}$ cm/sec. If this is a continuous horizon, it could reasonably serve as a liner to retard PCB migration into deeper ground water zones. As a precaution and to preserve the integrity of the horizon, the stratigraphic borings did not penetrate more than three feet into this clay.

Fill materials encountered in the 19 test wells were consistently mixed. Pieces of brick, lumber, cloth, metal, and concrete were encountered at any depth in any well. If continuous zones of coarse material are present, they may present preferred directions of migration for the water and oil. A cross-section of the shallow site stratigraphy is presented as Figure 3.1.

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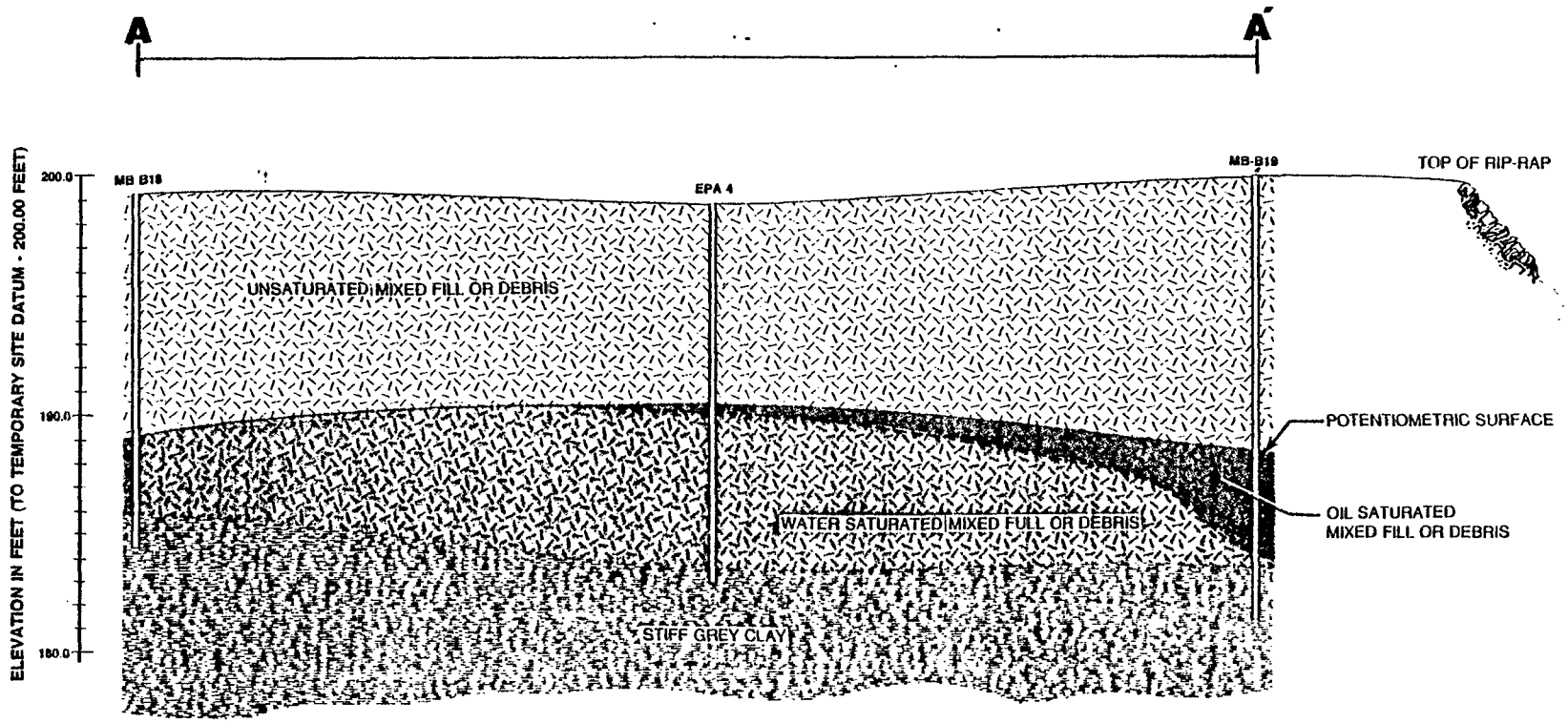
# TABLE 3.1

## WESTON PCB LABORATORY ANALYSES

| Laboratory Number | Description | Well Number | Date Sampled | Arochlor 1016/1242 | Arochlor 1248 | Arochlor 1254 |
|---|---|---|---|---|---|---|
| 5052 | Surface Soil Sample | MBS-1 | 4/12/78 | 1.35 ppm | | 0.48 ppm |
| 5053 | Surface Soil Sample | MBS-2 | 4/12/78 | 0.54 ppm | | |
| 5054 | Surface Soil Sample | MBS-3 | 4/12/78 | 7.8 ppm | | |
| 5055 | Surface Soil Sample | MBS-4 | 4/12/78 | 3.08 ppm | | |
| 5056 | Surface Soil Sample | MBS-5 | 4/12/78 | 3.6 ppm | | |
| 5057 | Surface Soil Sample | MBS-6 | 4/12/78 | 32.6 ppm | | |
| 5058 | Surface Soil Sample | MBS-7 | 4/12/78 | 4.3 ppm | | |
| 5059 | Surface Soil Sample | MBS-8 | 4/12/78 | 4.6 ppm | | |
| 5060 | Surface Soil Sample | MBS-9 | 4/12/78 | 13.5 ppm | | |
| 5061 | Surface Soil Sample | MBS-10 | 4/12/78 | 3.6 ppm | | |
| 5985 | Well Water | Well MB-81 | 5/25/78 | 32 ppb | | |
| 5986 | Well Water | Well MB-82 | 5/26/78 | | | 104 ppb |
| 5987 | Well Water | Well MB-83 | 5/25/78 | 101.5 ppb | | |
| 5988 | Well Water | Well MB-84 | 5/25/78 | | 35.8 ppb | |
| 5989 | Well Water (oil) | Well MB-85 | 5/26/78 | | | 780 ppm |
| 5990 | Well Water (oil) | Well MB-86 | 5/25/78 | | | 1570 ppm |
| 5991 | Well Water (oil) | Well MB-87 | 5/25/78 | | | 1280 ppm |
| 5992 | Well Water | Well MB-88 | 5/25/78 | 104 ppb | | |
| 5993 | Well Water | Well MB-89 | 5/26/78 | 21 ppb | | |
| 5994 | Well Water | Well MB-810 | 5/25/78 | 42.4 ppb | | |
| 5995 | Well Water | Well MB-811 | 5/25/78 | 31.4 ppb | | |
| 5996 | Well Water | Well MB-812 | 5/26/78 | | | 79.6 ppb |
| 5997 | Well Water | Well MB-813 | 5/26/78 | N.D. | | |
| 5998 | Well Water | Well MB-815 | 5/25/78 | N.D. | | |
| | | | | | | EPA-2 |
| 5999 | Soil Sample (3.5-5.0') | Well MB-85 | 5/16/78 | | 22.6 ppm | 2-4 8.2 ppm |
| 6000 | Soil Sample (8.5-10.0') | Well MB-85 | 5/16/78 | 46.3 ppm | | 6-8' N.D. |
| 6001 | Soil Sample (10.0-11.5') | Well MB-85 | 5/16/78 | 17.8 ppm | | 10-12' 16.4 ppm |
| 6435 | Well Water | Well MB-816 | 6/16/78 | 314 ppb | | |
| 6436 | Well Water | Well MB-817 | 6/16/78 | N.D. | | |
| 6437 | Well Water | Well MB-819 | 6/16/78 | 82 ppb | | |
| 6438 | Well Water | Well EPA 4 | 6/16/78 | N.D. | | |
| 6015 | Vegetation: stems and leaves-Alfalfa Medicago (Meliotus) MBF-1 | | 5/25/78 | 3.9 ppm | | |
| 6016 | Vegetation: lower leaves - Sycamore, Platanus accidentalis MBF-2 | | 5/25/78 | 3.0 ppm | | |
| 6017 | Vegetation: lower leaves - Willow, Salix higra MBF-3 | | 5/25/78 | 4.2 ppm | | |
| 6018 | Stems and leaves - Bed Straw, Galium aparine MBF-4 | | 5/25/78 | 2.6 ppm | | |

Mean Concentration of PCBs in Ground Water 77.1 ppb

N.D. = Not Detected




NOTE: HORIZONTAL SCALE - 1" = 50'
SEE FIGURE 1.2 FOR LOCATION OF CROSS SECTION
MB-B19 - WELL DESIGNATION
FOR TEMPORARY SITE DATUM LOCATION REFER TO FIGURE 1.2

**FIGURE 3.1**
**CROSS SECTION THROUGH SITE**
**(SECTION AA')**
**21 JUNE 1978**

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## 3.3 HYDROGEOLOGY

### 3.3.1 Piezometric Surface and Ground Water Flow

The contour map of the top of the fluid surface shown in Figure 3.2 represents the piezometric surface of the oil or water surface as measured within one hour on 21 June 1978 (Table 3.2). It represents a low, rising tide condition. The predominant subsurface fluid gradient observed was toward the river. Ground water flow is perpendicular to the fluid level contours from higher to lower fluid elevations. Thus, a net discharge of ground water into the Delaware River is indicated.

Tidal influenced fluctuation was observed in the fluid surface and a continuous recorder was placed on one well (MB-B7) for 48 hours. River tidal range at the site is approximately 6.2 feet at mean tide and 6.5 feet at spring tide. During the period of continuous observation, the river was approaching spring tide conditions. Ground water level fluctuations observed were on the order of one-half foot.

#### 3.3.1.1 Rate of Ground Water Flow

The velocity of subsurface fluid flow can be computed by using the following relationship from the Darcy equation:

$$V = Ki \qquad \text{(Equation 1)}$$

where: V = ground water velocity (feet/day)

K = hydraulic conductivity of fluid (assumed to be water) (feet/day)

i = ground water gradient (feet/foot)

The K value was determined by conducting a "slug injection" test at Well MB-B7 and was found to be 8.62 feet/day. This K value is typical of water in a silt matrix. A gradient of $4.1 \times 10^{-3}$, measured from the contour map (Figure 3.2) was used in the calculation. Therefore, a groundwater flow velocity of 0.035 feet/day is expected (13 feet/year).

#### 3.3.1.2 Ground Water Discharge

From the fluid level contours in Figure 3.2, it can be seen that ground water discharge face is approximately 1,000 feet wide. The depth of ground water flow is about 5 feet. Therefore, a cross sectional flow area of shallow ground water was calculated to be 5,000 feet$^2$. Utilizing the Darcy equation of continuity:

$$Q = (V)\ (A)\ (7.48) \qquad \text{(Equation 2)}$$

where: Q = ground water discharge (gal/day)

V = Darcy velocity (feet/day)

A = cross sectional aquifer area (ft$^2$)

7.48 = conversion factor (ft$^3$/day to gal/day)

Table 3.2

Physical Characteristics of Wells Drilled

| Well No. | Surface Elevation[1] | Bottom Elevation[1] | Δ | Potentiometric Surface Elevation[1] | Oil Presence/ Thickness |
|---|---|---|---|---|---|
| MB-B1 | 199.4 | 184.4 | 15 | 189.0 | 0.1 |
| MB-B2 | 198.9 | 183.9 | 15 | 189.1 | 0.3 |
| MB-B3 | 198.4 | 186.8 | 11.6 | 189.3 | 0.2 |
| MB-B4 | 200.0 | 186.0 | 14 | 188.8 | 0.2 |
| MB-B5 | 199.6 | 187.6 | 12 | 189.7 | 2.1[2] |
| MB-B6 | 199.7 | 187.2 | 12.5 | 189.5 | 2.0[2] |
| MB-B7 | 199.6 | 186.1 | 13.5 | 188.2 | 3.2[2] |
| MB-B8 | 199.8 | 186.3 | 13.5 | 188.9 | N.D.[3] |
| MB-B9 | 199.9 | 184.9 | 15 | 190.3 | N.D.[3] |
| MB-B10 | 199.7 | 184.7 | 15 | 191.7 | N.D.[3] |
| MB-B11 | 199.5 | 185.0 | 14.5 | 192.0 | 0.3 |
| MB-B12 | 199.9 | 184.9 | 15 | 189.3 | N.D.[3] |
| MB-B13 | 198.9 | 183.9 | 15 | 187.6 | N.D.[3] |
| MB-B14 | 199.6 | 188.9 | 11 | 190.7 | N.D.[3] |
| MB-B15 | 200.1 | 190.1 | 10 | 196.5 | 0.3 |
| MB-B16 | 198.2 | 186.7 | 11.5 | 189.8 | 1.4 |
| MB-B17 | 197.7 | 185.2 | 12.5 | 188.9 | 0.1 |
| MB-B18 | 199.3 | 184.3 | 15 | 188.9 | 0.1 |
| MB-B19 | 199.9 | 181.4 | 18.6 | 188.5 | 5.1 |
| EPA-1 | 199.5 | 185.5 | 14 | 189.6 | 0.3 |
| EPA-2 | 199.4 | 187.4 | 12 | 189.4 | 0.2 |
| EPA-4 | 198.8 | 182.8 | 16 | 190.1 | 0.1 |

[1] elevations with respect to assigned site datum of 200,000 feet

[2] following oil thickness value indicates well bottomed in oil, total thickness unknown

[3] N.D. = Not Detected

Thus, 1,300 gallons of ground water discharges to the Delaware River each day, or approximately 480,000 gallons of ground water per year.

### 3.3.2 Oil Distribution

The thickness of oil in the monitoring points was observed at the same time the piezometric surface data was collected (Table 3.2). The results are shown as an oil isopach map of the site (Figure 3.3).

This map shows that the oil is concentrated in a lens which trends through observation points MB-B7, MB-B19, MB-B6, MB-B5 and MB-B16. This suggests that either there is a zone of preferred permeability in the subsurface through which the oil has migrated or there is a zone of low permeability material which is preventing the oil from moving further. A cross section through the axis of the oil body was prepared to illustrate the configuration of that body and its relationship to the water table confining zone, and ground surface. This section is presented as Figure 3.4.

The oil isopach map also displays a second, very thin, detached lens of oil in the northern corner of the site. Because this area of oil appears to be discontinuous with the major mass of subsurface oil, it is felt that it is unrelated to the main body of oil observed in the southern corner of the site.

#### 3.3.2.1 Flow of Oil

The viscosity of oil is greater than that of water, so the discharge velocity of oil would be significantly slower. Using the ratio of kinematic viscosities of oil ($\mu o$) and water ($\mu w$) as an indication of the relative velocities. At 60°F, the kinematic viscosity of water is $1.217 \times 10^{-5}$ ft$^2$/sec and medium fuel oil is $4.75 \times 10^{-5}$ ft$^2$/sec. This ratio is 0.256 so the expected flow velocity of the oil, from the Darcy equation, is approximately $9.0 \times 10^{-3}$ ft/day (3.3 ft/year):

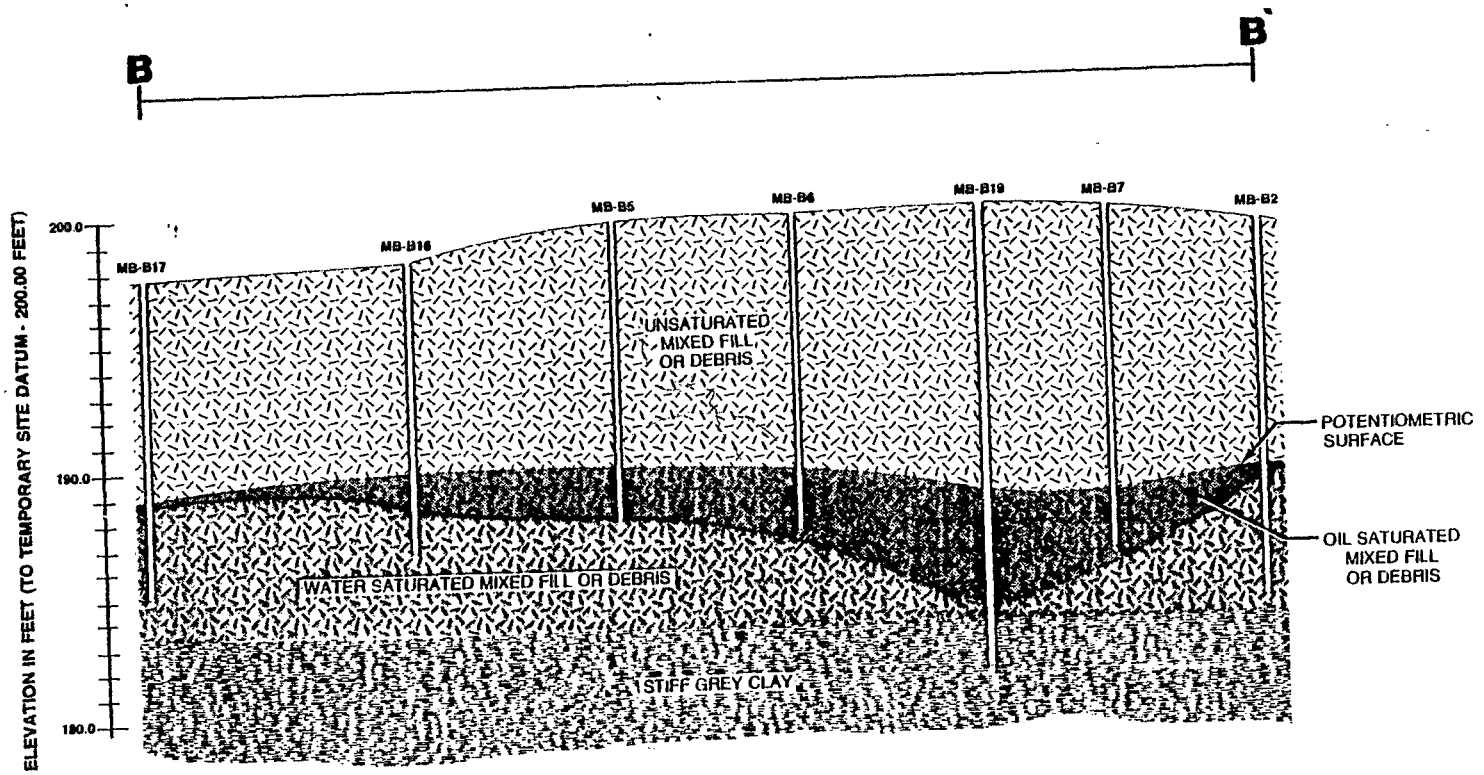
$$V = \frac{\mu w}{\mu o} \quad V \qquad \text{(Equation 3)}$$

#### 3.3.2.2 Oil Discharge

The subsurface oil discharges according to the Darcy equation of continuity (Equation 2). The cross sectional discharge area of the oil was found to be significantly less than that for ground water. Since the oil discharges as a slick, an estimate of oil discharge thickness is 0.5 mm. or $1.6 \times 10^{-3}$ ft. along the 500 foot seepage face (See plate 2.1).

$$Q = VA\ (7.48) \qquad \text{(Equation 2)}$$

$$Q = (9 \times 10^{-3})\ (1.6 \times 10^{-3})\ (5 \times 10^{2}) \times 7.48 = 0.05 \text{ gal/day}$$




NOTE: HORIZONTAL SCALE - 1" = 50'
SEE FIGURE 1.2 FOR LOCATION OF CROSS SECTION
MB-B19 - WELL DESIGNATION
FOR TEMPORARY SITE DATUM LOCATION REFER TO FIGURE 1-2

**FIGURE 3.4**
**CROSS SECTION THROUGH OIL LENS**
**(SECTION BB')**
**21 JUNE 1978**

WESTON

Utilizing equation 2 for oil discharge, approximately 0.05 gallon of oil per day, or 20 gallons of oil per year are expected to discharge from the site.

## 3.4 RESULTS OF PCB SAMPLING

Results of PCB sampling data are presented in Table 3.1. The areal distribution of these sample results are shown in the map Figure 3.5. Since PCB data collected by the EPA and other agencies had indicated very high levels of PCB in the subsurface oil fraction, only three samples of the oil fraction were analyzed for verification purposes. These samples were from Wells MB-5, MB-6 and MB-7. In these cases, the oils were extracted and analyzed as a separate fraction. The PCBs identified in the oils were Arochlor 1254.

### 3.4.1 PCBs in Oil

#### 3.4.1.1 Occurrence

From the oil thickness levels measured within the monitoring wells and the associated contours of oil thickness as shown in Figure 3.3, the volume of the subsurface oil spill may be calculated (Equation 4). The volume of the spill is computed from the following equation:

$$V = \sum_{x=1}^{n} (a_x W_x) \times \emptyset \times 7.48 \qquad \text{(Equation 4)}$$

where: $V$ = volume of the spill in gallons

$\sum_{x=1}^{n} (a_x W_x)$ = volume sum of the contours (in $ft^3$) ($57319\ ft^3$)

$\emptyset$ = porosity of the subsurface material containing the spill (5%) ← for fill vol.

7.48 = conversion factor from $ft^3$ to gallons

From this relationship, the total volume of oil presently in the ground is found to be up to 21,000 gallons.

The three Weston samples of PCBs within the body of the oil (Table 1, Samples 5989, 5990 and 5991) have a mean PCB concentration of 1210 ppm/l. Utilizing this concentration, the total weight of PCBs entrained in the oil has been computed from the following equation:

$$W_{PCB} = V \times \bar{C} \times 8.3 \times 10^{-6} \qquad \text{(Equation 3)}$$

Where: $W$ = weight of PCBs (in lbs)

$V$ = volume of oil computed above (21,000 gal)

$\bar{C}$ = avg. concentration (1210) ppm

$8.3 \times 10^{-6}$ = conversion factor (ppm/gallon to pounds of PCBs/gallon

Therefore, the total pounds of PCBs present in the oil on the site has been computed to be up to 215 lb.

### 3.4.2 PCBs in Ground Water

The natural solubility of PCBs in water is quite low. The higher chlorinated Arochlors 1248, 1254 have a maximum solubility of from 50 to 200 ppb, whereas the lower chlorinated Arochlor 1016 has a solubility of about 225 ppb. PCB analyses were made of the ground water sampled from the wells on the site (except MB-B5, 6 and 7 where only oil was collected).

#### 3.4.2.1 Occurrence

From the analyses shown in Table 3.1, the mean concentration of PCBs in the ground water beneath the site was found to be 77.1 ppb. The maximum concentrations of PCBs found in the ground water at the site were 314 ppb in Well MB-B16 and 104 ppb in Wells MB-B2 and MB-B8. All three of these wells lie in close proximity to the center of the spill. Figure 3.6 is a plot of the distribution of concentration of PCBs with distance from the center of the oil spill. This indicates that attenuation of PCBs in the ground water system is occurring. It further suggests that the primary source of PCBs in the ground water is the pool of PCB impregnated oil located in the southern corner of the site.

Partitioning of PCBs from the source oils to the surrounding ground water is the ratio of PCB concentration in the source and the concentration in the surrounding ground water. Utilizing the mean PCB values in the oils to the mean PCB concentration in ground water immediately surrounding the oil spill, this partitioning ratio has been found to be $1.1 \times 10^{-5}$. Partitioning ratios reported in the literature range from $10^{-3}$ to $10^{-5}$.

The fact that PCBs are found inland of the spill in environmentally significant concentrations is evidence that perhaps one of the following conditions exists at the site:

- The pool of PCB impregnated oil is or was not the only source of PCBs on the site.
- The PCB surface contamination zone has enlarged in area through volatilization, surface traffic, or other means.
- Tidal streaming has caused cyclic reversals of ground water flows during high tides.

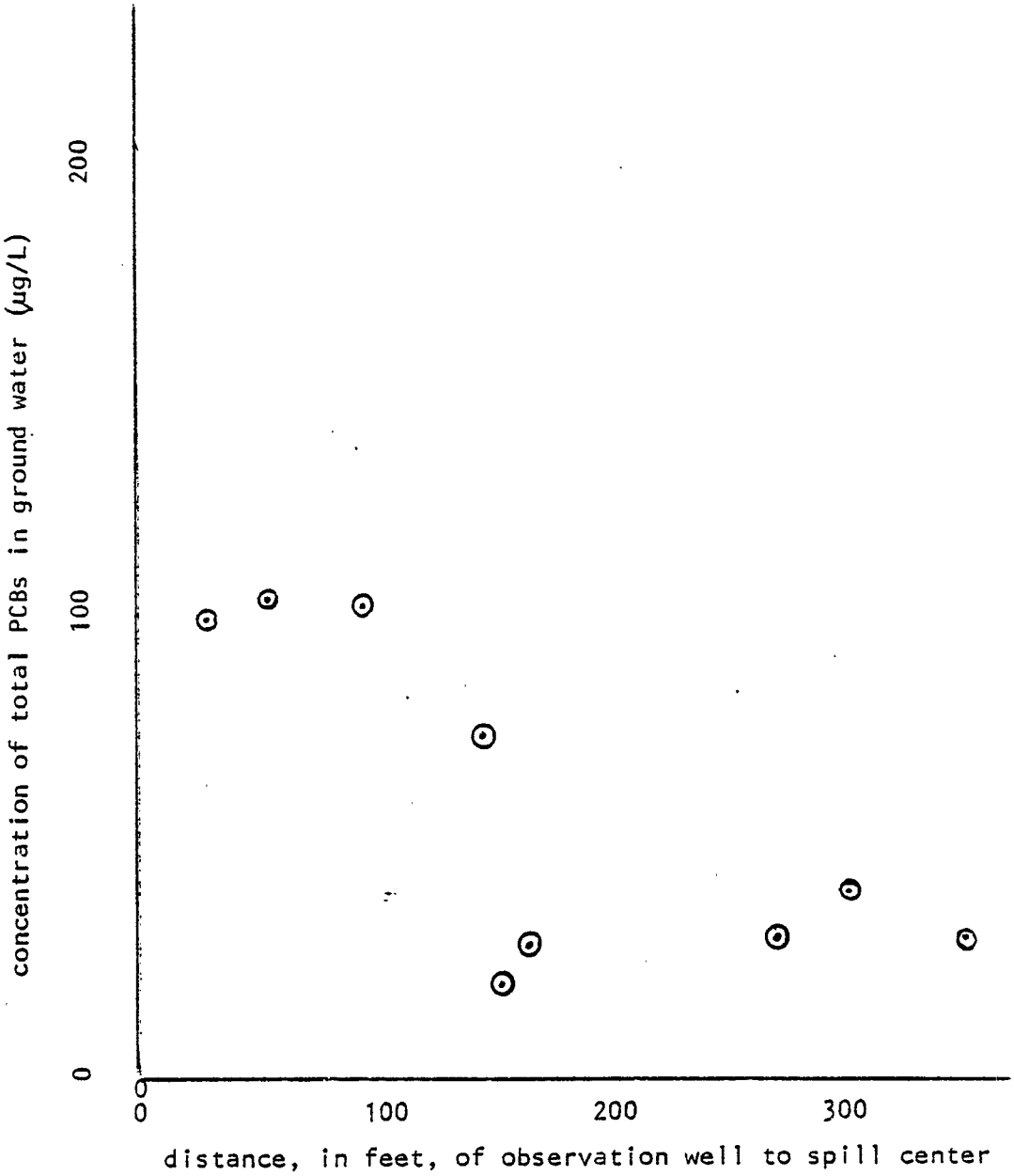
#### 3.4.2.2 PCB Migration in Ground Water

The migration of PCBs in the subsurface is controlled by four factors:

(1) The predominant discharge gradient;

FIGURE 3.6

Relationship Between PCB Concentration and Distance
From Center of Pool of PCB Impregnated Oil in
the Southern Corner of the Metal Bank of America
Cottman Avenue, Philadelphia, Pennsylvania Site



(2) The discharge velocity of the subsurface oil pool and the ground water;

(3) The permeability of the deposits through which it migrates; and

(4) The retardation of PCBs within the soil matrix.

Addressing these four factors at the Metal Bank of America site:

(1) The predominant discharge direction has been interpreted to be toward the Delaware River.

(2) The discharge velocity of the ground water and oil have previously computed to be .035 foot/day and $9 \times 10^{-3}$ foot/day, respectively.

(3) The permeability of the subsurface soils were measured at one point, Well MB-B7 and found to be 8.62 feet/day.

(4) The retardation of PCB mobility is a subject that is only recently being assessed by researchers. Retardation occurs with PCBs in the ground water. Since PCBs are fully soluble in the oil fraction, they will probably discharge to the river in proportion to their concentration in the oil slick being produced.

PCB flow retardation has been defined by numerous workers (Davidson and Genutchen, 1971; and Leis, et al., 1978). The empirical relationship has been defined as follows:

a. Migration Velocity of PCBs

$$V_{PCB} = \frac{\text{Darcy velocity}}{\theta \times R} \qquad \text{(Equation 6)}$$

$V_{PCB}$ = velocity of PCBs in feet/vear

Where: $\theta$ = the soil/water content fraction ($cm^3/cm^3$)

$R = 1 + \frac{P\ Kd}{\theta}$ = retardation factor

P = soil bulk density

Kd = adsorption coefficient of PCB ($cm^3/gm$)

References

Davidson J.M. and Genutchen, 1971, Migration of pesticides in Subsurface environments, Soils Science V.

Leis W.M., Beers W.F., Davidson J.M. and Knowles G.D., 1978. Migration of PCBs by Ground Water Transport - A Case of Twelve Landfills and Dredge Disposal Sites in the Upper Hudson Valley. New York, Proc. of First Annual Conference of Applied Research and Practice on Municipal and Industrial Waste Madison, Wisc., Sept. 10-13, 1978.

b. PCB Migration Potential

$M = Q/R \times C \times 8.33$ (Equation 7)

Where: M = PCB migration in pounds/year

Q = ground water flow in million gallons/year

C = average discharge PCB concentration in mg/l

R = retardation factor in the soil matrix

Since soil isotherm determination was not within the scope of this study, the values of the adsorption coefficient can only be estimated. A single representative basal soil sample was used to determine the total organic content. A relationship of Kd (the adsorption coefficient) to soil organic carbon content has been suggested by Weston researchers from soil isotherm data. A preliminary Kd value based upon a soil organic content of 10 percent was calculated. This value, although preliminary does provide an order of magnitude estimate of retardation.

3.4.2.3 Contribution to the Delaware River

Using these data, a sample estimate of: a) PCB migration velocity in feet/year and b) PCB loss in pounds/year was calculated, using Equation (7) above, as follows:

Ground water flow velocity = 13 feet/year

Ground water discharge = 0.48 million gallons/year

$\theta$ = .05 $cm^3/cm^3$ (sandy silt)

P = 2.0 $gm/cm^3$

$\bar{C}$ = 81 ppb (average concentration of PCBs from riverside wells MB-B2 to MB-B4)

= Kd = (calculated value based upon organic content of soil)

$R = 1 + \frac{P\ Kd}{\theta} = 1001$

a) PCB flow velocity (Equation 6)

$V_{PCB} = \frac{V\ Darcy}{Q \times R}$

= 0.26 foot/year

b) PCB loss potential (Equation 7)

$M = Q/R \times \bar{C} \times 8.33$

$= 3.2 \times 10^{-4}$ pounds/year

It must be stated that the PCB flow velocity is independent of the initial PCB concentrations while the PCB loss potential is a fraction of the initial

concentration of PCBs in the ground water at the source. Therefore, PCBs are migrating at the rate of 0.26 foot/year.

The purpose of determining retardation of PCB migration in soils at the Metal Bank site is to provide a realistic determination of the magnitude of the problem. The standard practice for determining concentrations of pollutants traveling in ground water is to use a mass balance approach, derived from the Darcy equations. Calculating PCB flow velocity and loss potential in terms of mass balance would result in a PCB migration rate of 13 feet per year and a PCB loss potential of 0.32 pound per year. Thus, using the PCB retardation formulas give a more realistic determination of the problem.

### 3.4.3 PCBs in Oil

Since PCBs are fully soluble in oil, they are expected to discharge to the river in approximately the same concentration that they are observed in the oil within the site. Since 20 gallons of oil have been calculated to discharge to the river each year, 0.2 pounds of PCB would be released to the river as a soluble fraction within the oil.

### 3.4.4 Total Oil and Waterborne Discharge of PCBs to the Delaware River

Based upon the previous calculation of the oil velocity discharging to the river, we estimate that less than 20 gallons of oil and about 0.2 pounds of PCBs discharges to the river each year. The ground water discharge to the Delaware River has been computed to be 480,000 gallons/year through the sediments and approximately $3.2 \times 10^{-4}$ pounds of PCBs would be contributed to the river by the ground water flow. These calculations are summarized in Table 3.3. It can be seen that the predominant contribution of PCBs is within oil seepage rather than ground water discharge.

TABLE 3.3

Summary of Calculated Parameters

| | | Oil | Ground Water |
|---|---|---|---|
| Fluid Flow Velocity | | $9 \times 10^{-3}$ feet/day | 0.035 feet/day |
| | | 3.3 feet/year | 13 feet/year |
| Discharge Area | thickness | 0.5 mm | 5 feet |
| | length | 500 feet | 1000 feet |
| | area | 0.8 feet$^2$ | 5000 feet$^2$ |
| Discharge to Delaware River | | 0.05 gallons/day | 1300 gallons/day |
| | | 20 gallons/year | 480,000 gallons/year |
| Volume on site | | 21,000 gallons | - |
| Average PCB Concentrations at Discharge | | 1210 ppm | 81 ppb |
| Pounds of PCBs in Oil | | 215 pounds | - |
| PCB Migration Velocity in Water | | | 13 feet/year (mass balance)<br>0.26 feet/year (PCB retardation considered |
| PCB Discharge to Delaware River | | 0.2 pounds/year | 0.32 pounds/year (mass balance)<br>$3.2 \times 10^{-4}$ pounds/year (PCB retardation considered |

# SECTION 4

## PROJECT CONCLUSIONS

- An oil spill at the Metal Bank of America has been investigated by the EPA and DER and found to contain PCBs. Weston data confirms that PCBs are present.

- At the Metal Bank property, a subsurface oil pool was encountered. Based upon piezometric data, the volume of this pool was computed to be up to 21,000 gallons. Average PCB concentrations in samples tested indicate that approximately 215 pounds of PCBs are entrained in this oil.

- The PCB contaminated oil has released PCBs to the underlying ground water with an oil to water partitioning ratio of $10^{-5}$. This is consistent with partitioning ratios in similar situations.

- Utilizing Darcy flow relationship and a preliminary retardation equation, $3.2 \times 10^{-4}$ pounds of PCBs are released each year from the site by ground water discharge and 0.2 pounds by oil discharge.

- It is apparent that the oil discharge is a greater PCB threat to the Delaware River than the ground water discharge. The pool of oil also provides continuing source of PCBs to the ground water, hence to the Delaware River via that route.

- The zone of ground water contamination by PCBs extends through the property boundary and, from data acquired, probably extends beyond the Metal Bank of America property line. Concentrations in ground water vary between 104 ppb near the oil pool to 31.4 ppb near the property line.

- PCB concentrations in terrestrial plants sampled varied from 2.6 to 4.2 ppm, indicating biologic uptake through plant roots and/or volatilization of PCBs from the site.

# SECTION 5

## CONCEPTUAL AND SITE SPECIFIC CONTROLS

On 8 February 1978, regulations governing the labelling and disposal of PCBs were promulgated. All PCB liquids drained from transformers or from large high and low voltage capacitors are required to be disposed of by high temperature incineration. Until 1 January 1980, large capacitors may be placed in chemical landfills. Drained transformers, dredge spoil, municipal sewage sludge and materials contaminated by spills must be disposed of either by incineration or by placement in a chemical landfill. As part of these regulations, on 30 May 1978 a PCB concentration of 50 ppm for any mixture containing PCBs is defined as the level below which prescribed disposal provisions will not be required. According to memoranda from the EPA Assistant Administrator, the 50 ppm limit was set despite the fact that "it is apparent that there is no finite level at which continuing release into the environment could be regarded as insignificant". Of major importance to the Metal Bank study is a section of these regulations that allows the use of chemical waste landfills for disposal of soil and debris contaminated with PCBs, whether as a result of a spill or from placement of PCBs in a disposal site prior to the effective date of the regulations.

In the light of this regulation, it has become even more important to prevent continued discharge of PCBs from the Metal Bank site because the volume of discharge is more than 0.2 pound per year. There are a number of engineering options to effect this ranging from removal of all PCB contaminated materials for incineration or placement in secure chemical landfills to the more cost-effective option of removal of the source oil and ground and surface water control. This section includes general descriptions of the attenuation or control methods available prior to discussing a recommended option.

### 5.1 DEVELOPMENT OF CONCEPTUAL CONTROLS

As part of the engineering effort for this project, Weston developed four conceptual control options which could substantially decrease the discharge of PCBs to the environment, in particular to the Delaware River. These conceptual control options are:

- Removal of PCB source
- Inflow reduction
- Outflow control
- Area management.

These controls all focus on meeting the goals of: limiting the quantity of water entering the PCB disposal site, treating any waters leaving the site and developing a program for evaluation of the controls implemented.

### 5.1.1 Removal of PCB Source

Removal of the source of PCBs is the most important aspect of control at the Metal Bank site. Since the PCB source material is a subsurface pool of oil that is discharging slowly to the Delaware River, it is feasible to remove these oils by subsurface pumping. In order to minimize contaminated oil/water emulsions, a low rate interference pumping scheme would be initiated. Such a scheme would utilize large (greater than or equal to 12 inches) diameter wells outfitted with shallow draft sump pumps.

Recent developments in oil control technology may permit high rate pumping from smaller well points and surface treatment of the oil/water mixture as a cost effective procedure. Separating the oils from the water is readily achieved, but the problem of disposal of the PCB-containing water remains.

The PCBs would be collected for disposal (in EPA-approved disposal options) by means of on-site surface storage equipment. Since some emulsification will be present, a decant of water through PCB absorbent material would be required. Again, disposal of PCB contaminated water and/or absorbent materials must be considered in the total cleanup effort.

The success of the cleanup method selected would be dependent upon:

- Proper design and construction
- Careful maintenance during operation
- Periodic sampling of effluents.

### 5.1.2 Inflow Reduction

In general, inflow reduction is a control strategy composed of one or more of the following approaches:

- Diversion of off-site runoff
- Placement of impermeable cover over the PCB disposal site
- Diversion of ground water which would flow through the site
- Land surface management to remove PCB sources.

The common purpose of each of these approaches is to minimize the amount of water (surface water and ground water) entering the PCB disposal site.

Diversion of off-site runoff is the interception and routing of any surface water (from precipitation) that would otherwise flow onto the PCB disposal site. Interception and routing can be accomplished by utilizing lined (stone) ditches. This off-site runoff should not contain any PCBs and treatment (if required at all) would be dependent upon the level of suspended solids contained in the flow.

Placement of an impermeable cover over the PCB disposal site will reduce the infiltration of precipitation. This control attains three goals: it reduces the quantity of water entering the site from above and eliminates the downward driving force that would push contaminated water from the site in the form of seeps or into the ground water; through physical separation, it reduces the potential for contamination of surface water runoff and, through physical separation from the atmosphere, it eliminates the potential for volatilization of PCBs. Many materials, both natural (e.g. various clays) and synthetic (e.g. PVC, 3110, Polyethylene, Hypalon, etc.) are readily available.

Diversion of ground water that flows into a PCB disposal site eliminates a major potential source for the migration of PCB contaminated waters from a site. The inflow of ground water into a PCB disposal site can be a significant source of water in which PCBs may be dissolved or materials containing PCBs may be suspended. Also, ground water inflow provides a force to drive contaminated waters from the site. The technology for diversion of ground water is readily available and well proven, having been used for many years in the construction industry. Existing technology includes: well points, trenches, grouting and sheet piling.

Each of the three strategies is designed to control a specific component of the water balance on the site. If used concurrently, they will assure almost complete isolation of the site.

If an impermeable cover is not utilized, then it is essential that proper surface management be practiced. Such procedures should be followed even if an impermeable cover is utilized. Proper surface management consists essentially of two elements:

- Grading the surfaces to a uniform slope to minimize erosion, ponding and infiltration/percolation.

- Fertilizing and seeding the surface to establish a proper vegetative cover. Such a cover (e.g. Reed Canary Grass) will aid in erosion control and reduce infiltration/percolation through the evapotranspiration process.

### 5.1.3 Outflow Control

Even if all the inflow reduction control strategies were implemented, there will still be some water leaving the Metal Bank site due to tidal effects. For adequate protection of the environment, it is essential that these waters be collected, monitored and treated. There are four elements to a program for successful control of the outflow from a PCB disposal site:

- Collection of all surface runoff from the site
- Collection of all springs or seeps
- Treatment of collected waters and monitoring of the effluent
- Monitoring of ground water to record the quality.

Collection of all surface runoff and any seeps is accomplished by a lined (impermeable material, PVC, etc.) ditch completely encircling the PCB disposal site. The distance between this ditch and the actual site depends on the potential for seeps to occur and on the probable locations of the such outflows, as it is essential that these be collected. This ditch will be placed on the site side of the off-site runoff diversion ditch and only a short distance (e.g. 10 feet) is required for separation. The collection ditch is sloped in such a manner that it will transport the collected waters to a sedimentation basin.

It has been reported that PCBs have a high affinity for suspended materials and that the quantity actually dissolved in the water will be something less than 250 ppb (PCB solubility limit in water); therefore, an effective treatment method is to remove the suspended materials in a sedimentation basin with discharge of the effluent to the natural drainage systems. If additional treatment is required, it is possible to add activated carbon to the sedimentation basin to achieve higher removals, but this may be limited by economic considerations. The material which collects in the basins is periodically dredged and placed in a PCB disposal site.

To evaluate such a treatment system properly, a monitoring program will have to be implemented. Samples of effluent from the sedimentation basin will have to be collected and analyzed for suspended solids and for filtered and unfiltered PCBs. Also, a ground water monitoring system will have to be implemented to insure that the control options are effective and that no waters or other materials containing PCBs are being discharged to the ground water. This monitoring system, at a minimum, would consist of two background wells (upgradient from the site) and three quality wells (downgradient from the site).

### 5.1.4 Area Management

The third control concept developed in this study is area management. This does not have the same potential for significantly reducing the quantities of PCBs released to the environment as the previous two concepts; nevertheless, it is very important to the overall PCB control program. There are three compenents to area management:

- Delineation of PCB disposal areas
- Long-term monitoring programs
- Maintenance of disposal sites

Delineation of areas containing PCBs is very important as they have been found to have chronic toxicity to both humans and animals. Access to these disposal sites should be limited and the sites should be clearly and permanently marked; fences with signs are recommended.

Adequate evaluation of the effects of the concepts implemented (treatment achieved, quantities of PCBs removed and quantities of PCBs released to the environment) requires extensive, long-term monitoring programs. This should include monitoring of soils, ground water (including background), effluent from sedimentation ponds and any other factors determined to be pertinent.

Maintenance of the site is important to insure that the level of treatment specified and initially provided is not downgraded through deteriorating site conditions.

## 5.2 RECOMMENDED SYSTEM

In order to accomodate the strict requirements of new EPA regulations governing PCB collection and disposal, the recommended program at the Metal Bank site would require the following elements:

- Removal of the subsurface PCB source by controlled pumping of the contaminated oils
- Isolation of the site by a combination of inflow controls and/or outflow controls
- Continued site management.

Since the elements are presently within available technology, they should be incorporated into a detailed comprehensive site remedial plan to be instituted relatively soon.

As part of this remedial action that focuses on the oil spill underlying Metal Bank, the following tasks should be accomplished for ultimate cleanup:

- The present study has concentrated upon the spill area and discharge of PCBs from the site. It has become apparent that some of the spill has become incorporated into the river bottom sediments near the site. It is recommended that a series of systematically sampled river bottom sediments be analyzed for evaluation of PCB dispersion into the estuary.
- Continued monitoring be carried out at the site to evaluate the configuration of oil pool during cleanup.
- A systematic biotic survey to determine the PCB pathways and effects upon the local biota.

A complete set of the Chain of Custody Documents for Analyzed Samples is available from the U.S. Coast Guard.

# Appendix B

## Laboratory Procedures

B.1 PROCEDURE FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYLS IN OILS

1) A 10 ml Aliquot of oil is placed on top of a micro column of florisil (which is prewet with henace).

2) 10 mls of hexane is applied to the column to eluate the saturated hydrocarbon fraction.

3) A second elution of 6% ethyl ether in hexane (10 mls) is used to eluate the polychlorinated biphenyl fraction.

4) The resuting eluate is subjected to gas chromatographic analysis and quantitation is adjusted via the appropriate dilution factor (usually 1000).

## B.2 PROCEDURE FOR THE DISOLUTION OF POLYCHLORINATED BIPHENYL FROM A PLANT FIBER MATRIX BY EXHAUSTIVE STEAM DISTILLATION

1) A representative sample of vegetation is dissected with sodium sulfate and ground to a powder.

2) An equivalent of one gram of original sample is transferred to a 100 ML conical flask with a t/s upper g round glass joint.

3) 50 mls of carbon filtered (PCB free) water is added .

4) The pH of the solution is adjusted to 11 .

5) The flask is fitted to a micro steam distillation condenser (similar to Vieths of USEPA).

6) 2 mls of toluene are charged into the apparatus.

7) The sample is allowed to distill for one hour.

8) The solvent layer is removed and placed into a 10 ml graduated cylinder.

9) The apparatus is washed 2x3 mls with toluene and the washings are added to the original toluene layer in the graduated cylinder.

10) The final volume is adjusted to 10 ml and the extract is subjected to gas chromatographic analysis.

The minimum detectable quantity of Aroclor1254 is approximately 50 mg/gr dry weight.

## B.3 THE SAMPLING AND ANALYSIS OF WATER FOR PESTICIDES

### I. INTRODUCTION:

The methodology for the analysis of water described in this section was researched by Thompson et al. at the Environmental Toxicology Division, Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC (1). It is based on modification of the multiclass, multiresidue procedure for pesticides in air reported by Sherma and Shafik in an earlier paper (2). Recovery studies were conducted on 42 halogenated compounds, 38 organophosphorus compounds, and 7 carbamates, and the procedure proved acceptable (> 80% recovery) for 58 of the 87 compounds tested. Thirteen compounds yielded recoveries exceeding 60%, while the remaining 16 compounds were recovered at levels below 60%. Concentration levels ranged from 0.09-400 ppb.

The present method provides the analyst with the means of simultaneously monitoring water samples for a wide variety of different pesticides, a capability not demonstrated for the few previously published under multiclass, multiresidue analytical procedures. For example, the method in the 1974 revision of this Manual included a Florisil cleanup column and was tested with only 16 organochlorine and 9 less-polar organophosphorus pesticides. Other published multiclass GC methods have employed cleanup on silica gel, Florisil, and alumina or no column cleanup. None of these is as broadly applicable as the following method.

REFERENCES:

1. Multiclass, Multiresidue Analytical Method for Pesticides in Water, Thompson, J. F., Reid, S. J., and Kantor, E. J., Arch. Environ. Contam. Toxicol., to be published in 1977.

2. A Multiclass, Multiresidue Analytical Method for Pesticide Residues in Air, Sherma, J., and Shafik, T. M., Arch. Environ. Contam. Toxicol. 3, 55 (1975). (See Section 8, this Manual).

3. Persistence of Pesticides in River Water, Eichelberger, J. W. and Lichtenberg, J. J., Environ. Sci. and Technol. 5(6), 541 (1971) (Table 1).

4. Pesticide Residue Analysis in Water--Training Manual PB-238 072, U.S. Environmental Protection Agency, OWPO, National Training Center, Cincinnati, Ohio, September, 1974, distributed by the National Technical Information Service, U.S. Department of Commerce.

5. Gas Chromatographic Determination of Residues of Methyl Carbamate Insecticides in Crops as their 2,4-Dinitrophenyl Ether Derivatives, Holden, E. R., J. Ass. Offic. Anal. Chem. 56, 713 (1973) and 58, 562 (1975).

II. PRINCIPLE: (See Schemes I and II, pages 16 and 17)

Compounds are extracted from water with methylene chloride, and the extract volume is reduced at low pressure and temperature in an evaporative concentrator. Compounds are separated into groups on a column of deactivated silica gel by elution with solvents of increasing polarity. Organochlorine compounds are determined by gas chromatography with an electron capture detector, organophosphorus compounds with a flame photometric detector, and carbamates by electron capture GC after conversion to 2,4-dinitrophenyl ether derivatives.

III. GRAB SAMPLE COLLECTION:

The sampling location and the method of drawing the sample will, to a great extent, be dictated by the objectives of the sample data. If the objective is to determine the highest pesticide pollution present in a stream or lake, a grab sample might be drawn at the point of highest pollution introduction. If, on the other hand, the objective is an average residue profile of the entire body of water, the final sample would preferably be a composite of a number of subsamples taken at various locations and water depths. If samples are collected in the area of a fish kill, a minimum of three samples are collected in the kill area, a control sample well above the suspected source of the pollutant, and one or two samples downstream of the kill area if the pesticide is downstream from the area of dying fish. In the case of a tidewater estuary, some modifications in the sampling pattern may be indicated.

As implied by the name, a grab or dip sample would be a surface water sample generally taken by simply filling the sample

container by immersing and allowing the bottle or jar to fill up. For sampling at selected depths, devices such as a Precision sewage water sampler or an Esmarch sampler may be utilized. Both devices consist of a metal outer container with a glass bottle inside as the sample collection vessel.

The Precision sampler in which the interior of the collection bottle has free access to the exterior by means of an open tube can be used to draw a composite depth sample. As soon as the device is immersed, collection of the sample is started. By premeasuring the rate of lowering the device to collect a given amount of water, an approximately uniform amount of water can be collected throughout the entire depth sampled.

The Esmarch sampler may be manually opened and closed by means of a chain attached to the bottle stopper. This permits a sample or subsample to be drawn from any given depth simply by lowering the device with the stopper closed, opening it at the proper sampling depth to permit filling of the collection bottle, then closing the stopper and raising the device to the surface.

IV. SAMPLE CONTAINERS AND STORAGE:

Wide mouth glass jars such as the Mason type are recommended as suitable sample containers when the sample is to be 2 liters or less. If the sample is of greater volume than 2 liters, the one gallon glass bottles in which acetone, hexane or petroleum ether are normally sold provide excellent sample containers. Furthermore, the latter require no special precleaning before use. Other glass containers must be scrupulously cleaned and rinsed with some of the same solvent used for subsequent pesticide extraction. All bottle or jar caps should be Teflon or foil lined to prevent contamination of the sample with trace quantities of impurities which may be present in laminated paper liners or in the composition of the material used for the seal in Mason jar lids.

The size of sample is dictated primarily by the expected residue levels. For example, if the sample is collected from a waterway where pesticide levels are expectedly high (such as agricultural run-off), a sample size of 500 to 1,000 ml may be sufficient. If the sample is drawn in connection with a monitoring program where no especially high residues would be expected, a sample size of 2 liters or more may be indicated. Sample containers should be carefully labeled with the exact site, time, date, and the name of the sampler.

Ideally, analysis of the sample should be conducted within a matter of hours from the time of sampling. However, this is frequently impractical in terms of the distance from sampling site to laboratory, and/or the laboratory workload. Samples being examined solely for organochlorine residues may be held up to a week under refrigeration at 2 to 4°C. Those intended for organophosphorous or carbamate analysis should be frozen immediately after drawing sample and should be extracted no more than 4 days after sampling. These classes of pesticides undergo degradation very rapidly in the aqueous medium.

Every effort should be made to perform the solvent extraction step at the earliest possible time after sampling, irrespective of the class of pesticides suspected as being present. The resulting extracts may then be held for periods up to three or four weeks at -15 to -20°C before conducting the adsorbent partitioning and determinative portions of the analysis. The reader is referred to Table 1 at the end of Section 10, A. These data show the degradation rate of 29 pesticides in water at ambient temperature in sealed containers (3).

V. OTHER SAMPLING METHODS (Reference (4), outline 22):

Continuous and automatic samplers of various types are appropriate for sampling flowing rivers and streams. Samplers have been designed to collect water samples at a rate proportional to either water flow or time. Equipment is now available for collecting proportionalized grab samples from gauged and instrumented streams that are proportional to the flow of the stream. This method is particularly useful, in fact required, to determine the total discharge load of a pesticide from a stream. For additional details, see reference (4), outline 22.

Carbon adsorption is a standard method for continuous sampling of water. The technique involves passage of a continuous, constantly controlled volume of water through a column of activated carbon. The major advantages of this method are that it takes a continuous sample and that it yields sufficient quantities of extract for corroborative, qualitative analyses.

The precision of the method appears to be satisfactory, but the quantitative efficiency is open to many questions. Efficiency of adsorption has already been found to vary dramatically,

depending on the rate of flow through the column and the total volume passed. A broad spectrum of organics are adsorbed by the carbon, but it has been estimated that perhaps 95% of the total organic load passes through. Many pesticides are adsorbed by activated carbon, but little is known at present about the efficiency of adsorption for specific pesticides. Quantitative statements of pesticide concentration based on carbon adsorption should be restricted to the "it is certain that no less than (X) amount was present," variety.

Besides carbon, many other filter materials have been recommended for continuous samplers, and continuous liquid-liquid extractors are also available.

VI. EQUIPMENT:

1. Gas chromatograph fitted with an electron capture detector and a flame photometric detector with a 526 nm P filter (thermionic detection may be substituted for the FPD). GC columns, borosilicate glass, 1.8 m x 4 mm i.d., packed with 1.5% OV-17/1.95% OV-210, and 5% OV-210, both coated on Gas-Chrom Q, 80/100 mesh, operated with specific parameters given under Gas Chromatography, Section IX. Criteria for high sensitivity in the GC system are set forth in Section 4, A, (4), page 4 for the E.C. detection mode, and in Section 4, B, (2), page 3 for the F.P.D. mode. These should be carefully noted.

2. Chromaflex columns, size 22, 7 mm i.d. x 200 mm, Kontes 420100.

3. Chromaflex column, 22 mm i.d. x 300 mm, size 241, Kontes 420530.

4. Rinco evaporator, rotating, such as Scientific Glass Apparatus Co. E-5500 or E-5500-1, with appropriate stand.

5. Variac or comparable voltage control regulator.

6. Water bath for operation at 35°C.

7. Vacuum source of 125 mm Hg, optimally.

8. Kuderna-Danish evaporators, 250 ml, Kontes 570001.

9. Centrifuge tubes, conical, 15 ml, graduated, Corning No. 8082 with Teflon lined plastic screw caps, thread finish 415-15, Corning 9998.

10. Tubes, culture, screw caps with Teflon liner, 16 x 125 mm, Corning 9826.

11. Evaporative concentrator tubes, 10 ml, graduated from 0.1 to 10.0 ml, size 1025 with outer joint T 19/22, Kontes 570050.

12. Tube heater with aluminum block containing 18 mm (3/4 inch) holes, Kontes 720000 (a water bath can be used as a substitute).

13. Mixer producing a tumbling action at ca. 50 r.p.m. (Fisher Roto-Rack or equivalent).

14. Prepurified nitrogen source with 3-stage regulation to produce a gentle stream of gas through an extruded tip of glass or stainless steel.

15. Vortex mini-mixer.

16. Disposable Pasteur pipets, Fisher 13-678-5A or equivalent.

VII. SOLVENTS AND REAGENTS:

1. Methylene chloride, hexane, benzene, acetonitrile, acetone, and methanol, all of pesticide quality.

2. Silica gel, Woelm, activity grade I, activated for 48 hours at 175°C before use. Prepare final deactivated material by adding 1.0 ml of water to 5.0 g silica gel in a vial with a Teflon-lined screw cap. Cap tightly and mix on the Roto-Rack for 2 hours at ca. 50 r.p.m. Discard deactivated silica gel after 5 days.

   NOTE: It is recommended that the amount of silica gel activated at 175°C be restricted to the quantity needed for immediate deactivation.

3. Sodium sulfate, granular, anhydrous. Purify by Soxhlet extracting with methylene chloride for ca. 60 discharge cycles.

4. 1-Fluoro-2,4-dinitrobenzene (FDNB), J. T. Baker 5-M478 or equivalent. Prepare a 1% reagent solution in acetone.

5. Sodium borate buffer, 0.1 M solution of $Na_2B_4O_7.10\ H_2O$, pH 9.4, J. T. Baker 3568 or equivalent.

6. Carborundum chips, fine. These should be purified as described for sodium sulfate in Item 3 of this section if a precheck indicates any contamination problems.

7. Glass wool, preextracted with methanol, acetone, and methylene chloride to remove any contaminants.

8. "Keeper" solution, 1% paraffin oil, USP grade, in hexane.

9. Eluting solutions:

   Fraction I - hexane

   Fraction II - benzene-hexane (60:40 v/v)

   Fraction III - acetonitrile-benzene (5:95 v/v)

   Fraction IV - acetone-methylene chloride (25:75 v/v)

10. Contaminant-free water. To 1500 ml of distilled water in a 2 L separatory funnel add 100 ml methylene chloride, stopper, and shake vigorously for 2 minutes. Allow the phases to separate, discard the solvent layer, and repeat the extraction with another 100-ml portion of methylene chloride. Drain the double-extracted water into a glass stoppered bottle for storage, withdrawing 500 ml to serve as a reagent blank with each set of samples.

11. Pesticide reference standards, analytical grade.

VIII. SAMPLE EXTRACTION AND CONCENTRATION:

1. Transfer 500 ml of water to a 1 L separatory funnel and add 10 g anhydrous sodium sulfate and 50 ml of methylene chloride. Shake vigorously for 2 minutes and allow a sufficient length of time for complete phase separation.

   NOTES: 1. If the expected pesticide concentration is extremely low, i.e., under .04 µg/L, it may be advisable to increase the initial sample to 1000 or 2000 ml. In this case, the volume of methylene chloride should be increased to 75 ml and the separatory funnel size to 2 or 3 L.

2. To avoid troublesome caking of the sodium sulfate at the bottom of the funnel, shaking should be conducted instantly after adding the sodium sulfate.

3. At this point a reagent blank of 500 ml of the preextracted water should be carried through all procedural steps in exactly the same manner as the sample(s).

2. Place a small wad of glass wool at the bottom of a 25 x 300 mm Chromaflex column and add a 2-inch depth of anhydrous sodium sulfate. Position the tip of the column over a Kuderna-Danish assembly consisting of a 250 ml K-D flask attached to a 10 ml evaporative concentrator tube containing two or three carborundum chips and 5 to 10 drops of keeper solution.

3. Drain the lower layer (methylene chloride phase) from the separatory funnel through the sodium sulfate column, taking care to avoid the transfer of any of the aqueous phase.

4. Add 50 ml more of methylene chloride to the aqueous phase in the funnel. Stopper and repeat the 2-minute shaking, phase separation, and draining of the organic layer through the sodium sulfate column into the K-D flask.

NOTE: It is not uncommon with highly polluted water samples to encounter persistent and sometimes severe emulsion problems at the methylene chloride-water interface. When this occurs, for example, in the extraction of some wastewater samples containing high surfactant concentrations, it is inadvisable to pass the methylene chloride phases through the sodium sulfate because the aqueous emulsion tends to clog the column and make filtration difficult. A good way to cope with an emulsion is to pack a filter tube (A. H. Thomas 4797-N15 or equivalent) with a 25 mm thick prewashed glass wool pad and pass the extract containing the emulsion through this filter into a 400 ml beaker, applying air pressure if necessary. If the emulsion persists on the second methylene chloride extraction, this treatment is repeated. The glass wool pad is

then rinsed with 25 ml of methylene chloride, collecting the extract and washing the beaker. Should there be evidence of water on the surface of the filtrate, a second glass wool filter is set up and the operation is repeated.

5. Connect the K-D flask to the rotary evaporator and incline the assembly to an angle approximately 20° from the vertical, with the concentrator tube about half immersed in a water bath previously adjusted to 35°C. Turn on the rotator, adjusting speed to a slow spin. Switch off the bath heat and apply vacuum to the evaporator at a pressure of ca. 125 mm of Hg.

   NOTE: The recommended adjustments of temperature, vacuum, and the pitch of the assembly should result in a steady boiling action with no bumping. The pitch should be such that no extract condensate collects in the lower position of the K-D flask. (See Figure 1).

6. Continue evaporation until the extract is condensed to ca. 4 ml, remove the assembly from the water bath, and rinse down the walls of the flask with 4 ml of hexane delivered with a disposable pipet.

7. Disconnect the concentrator tube from the K-D flask, rinsing the joint with ca. 2 ml of hexane delivered with a disposable pipet.

8. Place the tube under a gentle stream of nitrogen at ambient temperature and concentrate the extract to ca. 0.5 ml.

   NOTE: Under no circumstances should air be used for the blow-down as certain organophosphorus and carbamate compounds (and even low concentrations of some organohalogens) may not survive the oxidative effects.

## IX. SILICA GEL FRACTIONATION AND CLEANUP:

Before starting the following steps, place 10 drops of the paraffin oil-hexane keeper solution in the two 15 ml centrifuge tubes intended as the receivers for the eluates of Fractions III and IV.

1. Prepare a silica gel column as follows:

   a. Lightly plug a size 22 Chromaflex column with a small wad of preextracted glass wool.

   b. Add 1.0 g of deactivated silica gel, tapping firmly to settle, then top with 1-inch of anhydrous sodium sulfate and again tap firmly.

   c. Pass 10 ml of hexane through the column as a prewash, discarding the eluate.

2. When the last of the prewash hexane just reaches the top surface of the sodium sulfate, quickly place a 15 ml conical centrifuge tube under the column, and using a disposable pipet, carefully transfer the 0.5 ml of sample extract to the column. When this has sunk into the bed, rinse the walls of the centrifuge tube with 1.0 ml of hexane, and, using the same disposable pipet, transfer this washing increment to the column. Repeat this 1.0 ml hexane wash twice more and finally add 6.5 ml hexane to the column. The resulting 10 ml total effluent is Fraction I.

   NOTES: 1. There must be no interruption of the procedure during this step. Extreme care should be taken to apply the sample to the column at the precise moment the last of the hexane prewash reaches the top surface of the column.

   2. Faultless technique is required in this step to avoid any losses, particularly during the transfer of the 0.5 ml concentrated extract and the first rinse. All the pesticide derived from the original sample is concentrated in this very miniscule extract. The loss of one drop may introduce a recovery error of at least 10%.

3. Immediately position another 15 ml centrifuge tube under the column and pass through the column 15 ml of the benzene-hexane (60:40 v/v) eluting solution. This is the Fraction II eluate.

4. Make a third elution with 15 ml of the acetonitrile-benzene solution (5:95 v/v). This eluate is Fraction III.

5. A fourth elution fraction is necessary if there is reason to suspect the presence of crufomate, dicrotophos, dimethoate, mevinphos, phosphamidon or the oxygen analogs of diazinon and malathion. The elution solution is 15 ml of acetone-methylene chloride (25:75 v/v). This is Fraction IV.

6. Place the eluates under a gentle nitrogen stream at ambient temperature and concentrate as follows:

   a. Fractions I and II to ca. 3.0 ml, rinse down the tube sidewalls with ca. 1.5 ml hexane and adjust the volume to exactly 5.0 ml with hexane. Cap the tubes tightly and mix on the Vortex mixer for one minute.

   b. Fractions III and IV to 0.3 ml, rinse tube sidewalls with hexane, and dilute back to exactly 5.0 ml with hexane.

      NOTE: Fractions III and IV contain eluant solvents which may interfere in the GC determination, whereas those solvents in Fractions I and II would create no such problems. For this reason, Fractions III and IV are reduced to a lower volume to remove the original solvents.

7. Fractions II and III may contain carbamates as well as organophosphorus compounds. Gas chromatography of organophosphorus compounds by flame photometric detection is conducted on the eluates adjusted to 5.0 ml. When this has been completed, the tubes are placed back under a nitrogen stream, and the eluates are concentrated to 0.1 ml preparatory to derivatization of the carbamates which may be present.

   NOTE: The principal reason for concentrating this eluate to 0.1 ml is to reduce the volume of benzene which could interfere in the subsequent derivatization reaction.

X. CARBAMATE DERIVATIZATION:

1. Add 0.5 ml of the FDNB-acetone reagent solution and 5.0 ml of sodium borate buffer solution to the tubes containing the 0.1 ml of Fractions II and III, and add the same reagents to an empty tube to serve as a reagent blank.

NOTE: At this point, if any specific carbamate is suspected, prepare a solution of known concentration from a primary reference standard. A concentration of 5 µg per ml in acetone may be appropriate. This should be carried through the entire procedure starting with this step in exactly the same manner and at the same time as the unknowns.

2. Cap the tubes tightly and heat at 70°C for one hour in the heating block or in a water bath.

3. Cool the tubes to room temperature and add 5.0 ml hexane to each tube. Shake vigorously for 3 minutes, either manually or on a wrist action mechanical shaker.

4. Allow the layers to separate and carefully transfer 4 ml of the hexane (upper) layer to a vial or test tube which can be stoppered tightly.

XI. GAS CHROMATOGRAPHY:

For multiresidue analysis of samples with unknown pesticidal contamination, two GC columns yielding divergent compound elution patterns will aid confirmation. Two such columns are 5% OV-210 and 1.5% OV-17/1.95% OV-210. For EC detection, the column oven should be set at 200°C for the mixed column and at 180°C for 5% OV-210 (see exception for carbamates given under XI, 5). Carrier gas flow should be set to produce an absolute retention time of 16-19 minutes for p,p'-DDT.

Sensitivity levels for both EC and FPD detectors should be carefully established before starting chromatographic determination. The majority of water samples will contain extremely low pesticide concentrations, and, therefore an insensitive GC system will severely handicap the analysis. See Sections 4A and 4B of this manual for recommended criteria.

The majority of the halogenated pesticides will be found in Fractions I and II, with a few of the more polar compounds in Fraction III. Most of the organophosphorus compounds will be in Fractions II and III, none in Fraction I, and a very few in Fraction IV. Carbamates are eluted in Fractions II and III (Tables 2-4).

The analyst is referred to Section 4,A(4) of this Manual, pages 2 and 3, 12/2/74 revisions, for a time-saving procedure for tentative peak identification and choice of quantitation standards.

A number of organophosphorus compounds chromatographed with the FPD detector require considerable column preconditioning by repetitive injection of standards of relatively high concentration before attempting quantitation. Failure to carefully monitor linearity of response may result in erroneous quantitative values.

Typical gas chromatograms of silica gel column fractions are shown in Figures 2-4. Figure 3 illustrates the electron capture gas chromatography of chlorinated pesticides, Figure 4 the chromatography of organophosphates with FPD detection, and Figure 2 a chromatogram of dinitrophenyl ether derivatives of carbamates detected by electron capture.

## XII. RECOVERY AND DETECTION DATA:

Recovery data for the extraction step alone and the total procedure including silica gel chromatography, and the concentration levels tested are shown in Tables 2-4. Water samples of 500 ml are suitable for detection at these concentration levels. Of the 42 halogenated compounds evaluated, reproducible recoveries of 80% or more were obtained for 31. Gas chromatography linearity problems were encountered with captan and folpet, and a sizable portion of lindane was lost during silica gel fractionation.

Thirty one of the 38 organophosphorus compounds were recovered in the 80+% range and six between 60 and 79%. Reproducible and satisfactory recoveries were not achieved for carbophenoxon, disulfoton, methamidophos, monocrotophos, and oxydemeton methyl. Of these five compounds, excellent extraction efficiency was observed for carbophenoxon and disulfoton, but complete loss was experienced on the silica gel column. Six compounds were partially recovered in the 0-60% range. Of the 17 OP compounds yielding total recoveries of less than 80%, six of these gave over 90% extraction recovery, but losses occurred during silica gel chromatography.

Final recoveries after fractionation were acceptable for the carbamates metalkamate, carbofuran, methiocarb, and propoxur. Acceptable recoveries were obtained for aminocarb and carbaryl by direct derivatization and gas chromatography of the concentrated

methylene chloride extract, by-passing silica gel fractionation which caused losses for these two compounds. Recoveries of mexacarbate were highly inconsistent, both for direct analysis of spiked methylene chloride or water extracts. Silica gel fractionation of this compound resulted in further losses.

XIII. MISCELLANEOUS NOTES:

1. The recommended operation of the concentrator shown in Figure 1 is unusual for pesticide analysis. Customarily, solvent evaporation is achieved by immersing the concentrator tube in a water bath at a higher temperature than the boiling point of the solvent, or the flask is attached to a conventional rotary evaporator. The system shown in Figure 1 achieves two important objectives: the extract is exposed to a maximum temperature of less than 35°C to minimize degradation of heat labile compounds; and the concentrated extract is confined to one container, thereby eliminating need for a transfer. Using the temperature and vacuum levels specified in Section VIII, 100 ml of methylene chloride extract can be reduced to 5 ml in ca. 20 minutes in this apparatus.

2. The activity and performance of deactivated silica gel changes in a matter of days. It is desirable to deactivate only the amount required for a 2 or 3 day period. Continuous storage of activated silica gel at 175°C may result in a shift of the compound elution pattern of deactivated columns prepared from this adsorbent. The quantity of silica gel activated should be limited to a one week supply.

3. The derivatization procedure for carbamates is based on work reported by Holden (5) wherein phenols were formed by hydrolysis in a borate buffer followed by reaction with FDNB to form 2,4-dinitrophenyl ethers. This procedure is superior to derivatization with pentafluoropropionic anydride, as used by Sherma and Shafik (2). With the latter method, considerable masking of derivative peaks by EC detection is observed, and, in addition, most of the peaks elute so early and are so poorly resolved that quantitation is difficult. The Holden method of reaction of intact carbamates with FDNB reagent produces peaks which elute significantly later than those resulting from reagent impurities or other contaminants (Figure 4).

4. Recoveries of OP pesticides were found, in general, to be far better when methylene chloride-extracted water rather than unextracted distilled water was used as the spiking substrate to evaluate this procedure. Therefore, unextracted distilled water was used for all recovery studies. As a further test, a sample of water was obtained a few hundred yards downstream from the outfall of a large chemical manufacturing plant and was fortified with a mixture of pesticides and analyzed using the extraction and silica gel fractionation steps. Although a few extraneous peaks were observed with the electron capture detector, no significant interference with pesticide peaks occurred. This indicates the applicability of the method to real-life water samples.

5. The OV-210 GC column oven can be operated at an elevated temperature (e.g., 215 to 220°C ) to expedite elution of the carbamate DNFB derivatives which have high retention times.

XIV. ANALYTICAL QUALITY CONTROL:

1. It is strongly recommended that selected analytical grade standards of known concentrations be analyzed in parallel in each individual sample or set of samples. This will increase confidence in qualitative and quantitative results and will alert the analyst to any shifts in the compound elution pattern from the silica gel column. Certain compounds may elute in different fractions than those shown in Tables 2-4 when different lots of silica gel are used or as atmospheric conditions, particularly relative humidity, vary.

2. Interpretation of chromatograms should be carefully made, based on elution patterns from the two dissimilar GC columns and detectability by the EC and FPD detectors. Further confirmation of compound identity should be made by such techniques as TLC, microcoulometric or Coulson conductivity detector response, p-values, or coupled GC-MS if the latter equipment is available. Confirmatory procedures are discussed in Section 8 of the EPA Quality Control Manual.

# B.4 SAMPLE PREPARATION AND ANALYSIS OF SOILS AND HOUSE DUST

## I. INTRODUCTION:

The analytical method described below is similar in principle to the method presented in the Analytical Manual distributed at the annual Chemist's Meeting in Tucson in 1968. The main difference lies in the incorporation of the standard Mills, Onley, Gaither Florisil cleanup technique for which all laboratories have equipment and a degree of expertise in manipulation. This is preceded by percolation through an alumina column for further removal of contaminants.

## II. PRINCIPLES:

Organochlorine pesticides, together with other lipid-soluble substances, are extracted from homogenized samples by continuous Soxhlet extraction with acetone-hexane. Bulk of solvent is removed by evaporation in Kuderna-Danish equipment. Interfering lipid-soluble materials are then partially removed from the extracts by successive cleanup on aluminum oxide and Florisil columns. Extracts are adjusted to appropriate concentration for determinative analysis by E.C. and F.P.D., confirming as needed by M.C. and/or T.L.C.

## III. EQUIPMENT:

1. Soxhlet extraction apparatus, complete with 125-ml ℱ 24/40 flask, extraction tube with ℱ 24/40 lower and ℱ 34/45 upper joints and Friedrichs condenser with ℱ 34/45 joint. Kimble #24010 or the equivalent for the entire assembly.

2. Soxhlet extraction thimbles, paper, Whatman, 25 x 80 mm, Fisher #9-656-c or the equivalent.

3. Sieves, U. S. Standard, #10 mesh, #18 mesh and #60 mesh with top covers and bottom pans, 8" dia. x 2" depth, stainless steel.

4. Chromatographic columns, 22 x 300 mm with Teflon stopcock, without glass frit. Size #241, Kontes #420530 or the equivalent.

5. Kuderna-Danish concentrator fitted with grad. evaporative concentrator tube. Available from the Kontes Glass Company, each component bearing the following stock numbers:

   a. Flask, 250 and 500 ml, stock #K-570001.

   b. Snyder column, 3 ball, stock #K-503000.

c. Steel springs, 1/2", stock #K-662750.

d. Concentrator tubes, 10 ml grad., size 1025, stock #K-570050.

6. Modified micro-Snyder columns, 19/22, Kontes K-569251.

7. Glass beads, 3 mm plain, Fisher #11 - 312 or equivalent.

8. Evap. concentrator tubes, grad., 25 ml, ℱ 19/22, Kontes #570050.

9. Water or steam bath.

10. Glas Col heating mantles with variable autotransformers, size to match 125-ml Soxhlet flasks.

11. Filter paper, Whatman No. 1, 15 cm.

IV. REAGENTS AND SOLVENTS:

1. Acetone, pesticide quality.

2. Hexane, pesticide quality.

NOTE: Both solvents must be carefully checked for background contaminants as outlined in Section 3,C of this manual.

3. Extraction mixture - acetone/hexane, 1:1.

4. Aluminum oxide, Merck reagent grade, stock #71695 acid-washed. Prepare for use by shaking with 10% distilled water (w/w) for partial deactivation. Shelf life of 10 days if stoppered tight.

NOTE: The distilled water must be prechecked for contaminant background. If any interferences are detected, the water must be hexane extracted before use.

5. Diethyl ether - AR grade, peroxide free. The ether must contain 2% (v/v) absolute ethanol. Most of the AR grade ethyl ether contains 2% ethanol, added as a stabilizer, and it is therefore unnecessary to add ethanol unless peroxides are found and removed.

NOTE: To determine the absence of peroxides in the ether,

add 1 ml of ether in a clean 25-ml cylinder previously rinsed with ether. Shake and let stand 1 minute. A yellow color in either layer indicates the presence of peroxides which must be removed before using. See Misc. Note 4 at end of procedure. The peroxide test should be repeated at weekly intervals on any single bottle or can as it is possible for peroxides to form from repeated opening of the container.

6. Eluting mixture, 6% (6+94)-purified diethyl ether - 60 ml is diluted to 1000 ml with redistilled petroleum ether, and anhydrous sodium sulfate (10-25 g) is added to remove moisture.

7. Eluting mixture, 15% (15+85)-purified diethyl ether - 150 ml is diluted to 1000 ml with redistilled petroleum ether, and dried as described above.

NOTE: Neither of the eluting mixtures should be held longer than 24 hours after mixing.

8. Florisil, 60/100 mesh, PR grade, to be stored at 130°C until used. Furnished by Perrine on order.

NOTE: (1) In a high humidity room, the column may pick up enough moisture during packing to influence the elution pattern. To insure uniformity of the Florisil fractionation, it is recommended to those laboratories with sufficiently large drying ovens that the columns be packed ahead of time and held (at least overnight) at 130°C until used.

(2) Florisil furnished by the Perrine Laboratory has been activated by the manufacturer, and elution pattern data is included with each shipment. However, each laboratory should determine their own pesticide recovery and elution pattern on each new lot received, as environmental conditions in the various laboratories may differ somewhat from that in Perrine. Each new batch should be tested with a mixture of β-BHC, aldrin, heptachlor epoxide, dieldrin, p,p'-DDE, p,p'-DDD, and p,p'-DDT, eluting the standard mixture as described in Section 5,A,(1) of this manual. Dieldrin should elute entirely in the 15% diethyl ether fraction, whereas all other compounds should be in the 6% fraction.

9. Anhydrous sodium sulfate, reagent grade granular, Mallinckrodt

Stock #8024 or the equivalent.

NOTE: When each new bottle is opened, it should be tested for contaminants that will produce peaks by Electron Capture Gas Liquid Chromatography. This may be done by transferring ca 10 grams to a 125-ml Erlenmeyer flask, adding 50 ml pet. ether, stoppering and shaking vigorously for 1 minute. Decant extract into a 100-ml beaker and evaporate down to ca 5 ml. Inject 5 µl into the Gas Liquid Chromatograph and observe chromatogram for contaminants. When impurities are found, it is necessary to remove them by extraction. This may be done using hexane in a continuously cycling Soxhlet extraction apparatus or by several successive rinses with hexane in a beaker. The material is then dried in an oven and kept in a glass-stoppered container.

V. SAMPLE PREPARATION:

1. Soils and vacuum cleaner bag dusts are analyzed in the air-dry state. If a soil sample is obviously damp, it is allowed to equilibrate its moisture content with room air before handling. Trials have shown that house dust screenings generally contain approximately 0.1% moisture, possibly more in areas of high relative humidity.

2. Vacuum cleaner bag contents are sieved on U. S. Standard #10 and #60 sieves to remove hair, fibers and large particles. The resulting "fines" are separated into sealed glass jars until analyzed. Soils are sifted on a U. S. Standard #18 sieve to remove stones and other foreign material. Store the sieved soil in a sealed glass jar until analyzed.

3. The 15-cm filter paper and the Soxhlet extraction thimbles should be preextracted with the acetone/hexane extraction solvent prior to use. This may be conveniently done by folding several sheets of filter paper and placing in the Soxhlet extractor. Allow to cycle ca 2 hours, remove and dry. Wrap in aluminum foil and store in desiccator. The thimble is similarly preextracted and may be used repeatedly with no need for reextraction as long as it remains in good physical shape.

VI. EXTRACTION:

1. Weigh sample (2 grams of soil or 1 gram of dust) onto a sheet of 15-cm filter paper. Carefully fold paper to form a half-circle with the sample in the center (along the diameter line). Fold in the ends of the half-circle towards the center, the total resulting length to be ca 70 mm; then, starting at the diameter line, roll into an approximately cylindrical shape and insert into the extraction thimble.

2. As a recovery check, another portion of the same dust (or soil) should be spiked and carried through the entire procedure. This is done as follows:

   a. Weigh exactly 3.0 grams of the soil or 2.0 grams of dust into an evaporating dish. Add sufficient hexane to make a slurry.

   b. Prepare a standard mixture of the following compounds, the concentration expressed in micrograms per milliliter:*

| | | | |
|---|---|---|---|
| Lindane | 5.0 | Dieldrin | 7.5 |
| Hept. Epoxide | 5.0 | p,p'-DDD | 10.0 |
| Aldrin | 5.0 | o,p'-DDT | 10.0 |
| p,p'-DDE | 7.5 | p,p'-DDT | 10.0 |

   *In case your testing program indicates the presence of any other compounds or metabolites, standards of these should be included.

   c. Add 1.5 ml of this mixture to the soil sample or 1.0 ml to dust. Mix gently with a glass rod and evaporate the solvent at 40°C under a nitrogen stream, stirring from time to time.

   d. After removal of the solvent, allow the spiked sample to equilibrate to room temperature and humidity, and weigh the sample for extraction as outlined above in Step 1.

3. At this point, a reagent blank should be initiated, starting with the folded filter paper and carrying through the entire extraction, cleanup and determinative procedures.

4. Place the sample, reagent blank and spiked sample thimbles into separate Soxhlet extractors. Fill the boiling flasks, each containing six glass beads, about half full with the 1:1 acetone/hexane co-solvent, assemble the extraction apparatus, position in the heating mantles and start extraction.

NOTE: Each laboratory will need to determine the setting of their voltage controller. There should be sufficient heat to result in 1 discharge cycle about every 5 minutes, or ca 60 syphon discharges in a 5-hour period. This should be an adequate number of cycles to insure complete extraction.

5. At the completion of the extraction period disassemble the extraction apparatus, rinsing the joint between flask and extractor with a few ml of hexane.

6. Assemble a Kuderna-Danish evaporator with the 250-ml K-D flask attached to a 10-ml evap. concentrator tube containing one 3-mm glass bead.

7. Transfer the extract from the 125-ml Soxhlet flask to the K-D flask, rinsing the Soxhlet flask with 3 portions of 5 ml each of hexane. Attach the Snyder column and immerse evap. concentrator tube about 1-1/2 inches into the boiling water bath. Evaporate extract down to ca 3 ml, remove from bath and cool. Extract is now ready for cleanup.

I. ALUMINA AND FLORISIL PARTITIONING:

1. Prepare an alumina column as follows:

   a. Place a small wad of prerinsed glass wool at the bottom of a 22 x 300 mm chromatographic column.

   b. Add preextracted anhydrous $Na_2SO_4$ to a depth of 1/2 inch.

   c. Close stopcock and fill column with hexane.

   d. In a 50-ml grad. beaker, fill exactly to the 30 ml mark with alumina (this should be ca 30 grams). Add this slowly to the column, allowing all the alumina to settle to the bottom. Top this witl a 1-inch layer of $Na_2SO_4$. When settling is complete, open stopcock and allow the hexane to elute through the column down to a point ca 1/8 inch above the top of the upper $Na_2SO_4$ layer, then close stopcock.

      NOTE: This column packing technique minimizes the density that may be obtained in dry packing. The volume of hexane specified provides sufficient column prerinse.

2. Position a second K-D flask fitted with 10-ml evap. concentrator tube under column.

3. Transfer the 3 ml of concentrated extract from the first K-D evaporation to the column. Rinse tube with three portions of 3 ml each of hexane transferring the rinsings to the column.

4. Open stopcock and add 85 ml of hexane to the column, open stopcock wide and elute into the K-D flask.

5. Concentration of the eluate from the alumina column is conducted exactly the same as outlined above in Step 7 under Sample Extraction, taking extract down to 3 ml. This extract is now ready for Florisil partitioning.

6. Florisil column: Prepare the column as described in Section 5,A,(1) of this manual under FLORISIL FRACTIONATION, Steps 1 and 2, substituting hexane for pet. ether.

7. Assemble two more K-D apparatus but with 500-ml flasks and position the flask of one assembly under the Florisil column. However, at this point use 25-ml grad. evap. concentrator tubes instead of the 10-ml size for previous concentrations.

8. Using a 5-ml Mohr or a long disposable pipet, immediately transfer the extract from the evaporator tube in Step 5, above, onto the column and permit it to percolate through. Rinse tube with two successive 5-ml portions of hexane, carefully transferring each portion to the column with the pipet.

   NOTE: Use of the Mohr or disposable pipet to deliver the extract directly onto the column precludes the need to rinse down sides of the column.

9. Commence elution with 200 ml of 6% diethyl ether in pet. ether (Fraction I). The elution rate should be ca 5 ml per minute. When the last of the eluting solvent reaches a point ca 1/8 inch from the top of the $Na_2SO_4$ layer, place the second 500-ml Kuderna-Danish assembly under the column and continue elution with 200 ml of 15% diethyl ether in pet. ether (Fraction II).[1] Place both Kuderna-Danish evaporator assemblies in a water bath and concentrate extract to ca 20 ml.

   NOTE: If there is reason to suspect the presence of malathion in the sample, have a third 500-ml K-D assembly

ready. At the end of the 15% fraction elution, add 200 ml of 50% diethyl ether in pet. ether (Fraction III), evaporating the eluate in the same manner.

10. Remove K-D assemblies from bath, cool and rinse S joint between tube and flask with a little pet. ether. Finally, dilute both extracts to exactly 25 ml and proceed with the GLC determinative step.

NOTE: A relatively high dilution is suggested as it has been observed that residues are generally sufficiently high to warrant this. Furthermore, the concentration of contaminants remaining after cleanup is hereby reduced.

VIII. GAS CHROMATOGRAPHY:

1. Inject 5 µl of each fraction extract into the gas chromatograph (E.C. mode) primarily to determine whether the extracts will require further adjustment by dilution or concentration.

2. When appropriate dilution adjustments have been made in the extracts and column oven is set to a known temperature, the relative retention values of the peaks on the chromatograms should be calculated. When these values are compared with the values in the printed table for the appropriate column, the operator should be able to make tentative compound identifications. Microcoulometry and/or TLC may be required for positive confirmation of some of the suspect chlorinated compounds, whereas FPD may be utilized for the organophosphate suspects.

IX. ALUMINA COLUMN ELIMINATION:

It has been reported by several field scientists analyzing house dust that the alumina cleanup can be bypassed with no ill effects. In view of the expenditure of extra time and material, a laboratory conducting monitoring studies might find it advisable to make some recovery studies eliminating this step by taking the extract mentioned in Step 7 under EXTRACTION and starting the Florisil fractionation with Step 6 of subsection VII.

## B.5 SAMPLE PREPARATION AND ANALYSIS OF BOTTOM SEDIMENT

### I. INTRODUCTION:

The examination of sediment from the bottom of a stream or lake provides information concerning the degree of pollution resulting from pesticides, particularly the organochlorine compounds which are not readily biodegradable. This information combined with residue data obtained by analysis of the water and tissues from resident marine life contribute in the development of an overall profile of the pesticidal contamination of a given body of water.

REFERENCES:

1. Column Extraction of Pesticides from Fish, Fish Food and Mud, Hesselberg, R. J. and Johnson, J. L., in press.

2. Sediment Extraction Procedure, Southeast Water Laboratory, EPA, Athens, Georgia, Method Number SP-8/71.

### II. PRINCIPLES:

The sediment sample is partially dried and extracted by column elution with a mixture of 1:1 acetone/hexane. The extract is washed with water to remove the acetone and then the pesticides are extracted from the water with 15% $CH_2Cl_2$ in hexane. The extract is dehydrated, concentrated to a suitable volume, subjected to Florisil partitioning, desulfurized if necessary, and analyzed by gas chromatography.

### III. EQUIPMENT AND REAGENTS:

1. Pans, approximately 14" x 10" x 2-1/2".
2. Oven, drying.
3. Muffle furnace.
4. Desiccator.
5. Crucibles, porcelain, squat form, size 2.
6. Omni or Sorvall mixer with chamber of ca 400 ml.
7. Chromatographic columns, 300 mm x 22 mm with Teflon stopcock.

8. Separatory funnels, 500 ml and 250 ml with Teflon stopcocks.

9. Filter tube, 180 mm x 25 mm.

10. Kuderna-Danish concentrator fitted with grad. evaporative concentrator tube. Available from the Kontes Glass Company, each component bearing the following stock numbers:

    a. Flask, 250 ml, stock #K-570001.

    b. Snyder column, 3 ball, stock #K-503000.

    c. Steel springs, 1/2", stock #K-662750.

    d. Concentrator tubes, 10 ml, size 1025, stock #K-570050.

11. Pyrex glass wool - preextracted with methylene chloride in a Soxhlet extractor.

12. Hot water bath, temp. controllable at 80°C.

13. Sodium sulfate, anhydrous, Baker, prerinsed or Soxhlet extracted with methylene chloride.

14. n-Hexane, pesticide quality.

15. Acetone, pesticide quality.

16. Methylene chloride, pesticide quality.

17. Acetone-hexane, 1:1.

18. Diethyl ether, pesticide quality, free of peroxides.

19. Distilled water, suitable for pesticide residue analysis.

20. Sodium sulfate solution, saturated.

21. Methylene chloride-hexane, 15% v/v.

IV. SAMPLE PREPARATION AND EXTRACTION:

1. Decant and discard the water layer over the sediment. Mix the sediment to obtain as homogeneous a sample as possible and transfer

to a pan to partially air dry for about 3 days at ambient temperatures.

NOTE: Drying time varies considerably depending on soil type and drying conditions. Sandy soil will be sufficiently dry in one day, whereas muck requires at least three days. The silt and muck sediment is sufficiently dry when the surface starts to split, but there should be no dry spots. Moisture content will be 50-80% at this point.

2. Weigh 50 gm of the partially dried sample into a 400-ml Omni-Mixer chamber. Add 50 gm of anhydrous sodium sulfate and mix well with a large spatula. Allow to stand with occasional stirring for approximately one hour.

NOTE: As the final calculations will be made on a "bone dry" basis, it is necessary at this point to initiate the test for percent total solids in the sample being extracted for pesticide evaluation. Immediately after weighing the 50gm sample for extraction, weigh ca 5 gm of the partially dried sediment into a tared crucible. Determine the percent solids by drying overnight at 103°C. Allow to cool in a desiccator for half an hour before weighing. Determine the percent volatile solids by placing the oven-dried sample into a muffle furnace and igniting at 550°C for 60 minutes. Allow to cool in a desiccator before weighing.

3. Attach the 400-ml chamber to an Omni or Sorvall mixer and blend for about 20 seconds. The sample should be fairly free flowing at this point.

4. Carefully transfer the sample to a chromatographic column. Rinse the mixer chamber with small portions of hexane adding the rinsings to the column.

5. Elute the column with 250 ml of 1:1 acetone-hexane at a flow rate of 3-5 ml/min into a 400-ml beaker.

6. Concentrate the sample extract to about 100 ml under a nitrogen stream and at a temp. no higher than 55°C. Transfer to a 500-ml separatory funnel containing 300 ml of distilled water and 25 ml of saturated sodium sulfate solution. Shake the separatory funnel for two minutes.

7. Drain the water layer into a clean beaker and the hexane layer into a clean 250-ml separatory funnel.

8. Transfer the water layer back into the 500-ml separatory funnel and reextract with 20 ml of 15% methylene chloride in hexane, again shaking the separatory funnel for two minutes. Allow the layers to separate. Discard the water layer and combine the solvent extracts in the 250-ml separatory funnel.

9. Wash the combined solvent extract by shaking with 100 ml of distilled water for 30 seconds. Discard the wash water and rewash the extract with an additional 100 ml of distilled water, again discarding the wash water.

10. Attach 10 ml evap. concentrator tube to a 250-ml Kuderna-Danish flask and place under a filter comprised of a small wad of glass wool and ca 1/2 inch of anhydrous $Na_2SO_4$ in a filter tube.

11. Pass the solvent extract through the drying filter into the K-D flask, rinsing with 3 portions of ca 5 ml each of hexane.

12. Attach Snyder column to top joint of K-D flask, immerse tube in 80°C water bath and concentrate extract to 5 ml or to a lesser volume if extremely low concentration levels of pesticides are expected.

V. FLORISIL PARTITIONING:

Remove tube from water bath rinsing joint with a small volume of hexane. The partitioning is carried out as described in Section 11A, starting at VII., Step 6.

VI. GAS CHROMATOGRAPHY:

Again proceed as described in Section 11A.

VII. CALCULATIONS:

1. Percent Dry Solids

$$\frac{\text{gm of dried sample}}{\text{gm of sample}} \times 100 = \% \text{ Dry Solids}$$

2. Percent Volatile Solids

gm of dried sample - gm of ignited sample = gm of volatile solids

$$\frac{\text{gm of volatile solids}}{\text{gm of sample}} \times 100 = \% \text{ Volatile Solids}$$

3. Concentration of Pesticide in Sediment

% dry solids x 50 gm = gm of dry sample extracted

$$\frac{\text{1 of sample extract injected}}{\text{1 of sample extract}} \times \text{gm of dry sample extracted} = \text{gm of dry sample injected}$$

$$\frac{\text{ng of pesticide}}{\text{gm of dry sample injected}} = \text{ppb of pesticide}$$

VIII. SULFUR INTERFERENCE:

Elemental sulfur is encountered in most sediment samples, marine algae and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphate pesticides; therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. The sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorus mode, and Coulson electrolytic conductivity detectors. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through aldrin.

This technique eliminates sulfur by the formation of copper sulfide on the surface of the copper. There are two critical steps that must be followed to remove all the sulfur: (1) the copper must be highly reactive; therefore, all oxides must be removed so that the copper has a shiny, bright appearance; and (2) the sample extract must be vigorously agitated with the reactive copper for at least one minute.

It will probably be necessary to treat both the 6% and 15% Florisil eluates with copper if sulfur crystallizes out upon concentration of the 6% eluate.

Certain pesticides will also be degraded by this technique, such as the organophosphates, chlorobenzilate and heptachlor (see Table 1). However, these pesticides are not likely to be found in routine sediment samples because they are readily degraded in the aquatic environment.

If the presence of sulfur is indicated by an exploratory injection from the final extract concentrate (presumably 5 ml) into the gas chromatograph, proceed with removal as follows:

1. Under a nitrogen stream at ambient temp., concentrate the extract in the concentrator tube to exactly 1.0 ml.

2. If the sulfur concentration is such that crystallization occurs, carefully transfer, by syringe, 500 µl of the supernatant extract (or a lesser volume if sulfur deposit is too heavy) into a glass-stoppered, 12-ml grad., conical centrifuge tube. Add 500 µl of iso-octone.

3. Add ca 2 µg of bright copper powder, stopper and mix vigorously 1 minute on a Vortex Genie mixer.

   NOTE: The copper powder as received from the supplier must be treated for removal of surface oxides with 6N $HNO_3$. After about 30 seconds of exposure, decant off acid, rinse several times with dist. water and finally with acetone. Dry under a nitrogen stream.

4. Carefully transfer 500 µl of the supernatant-treated extract into a 10-ml grad. evap. concentrator tube. An exploratory injection into the gas chromatograph at this point will provide information as to whether further quantitative dilution of the extract is required.

   NOTE: If the volume transfers given above are followed, a final extract volume of 1.0 ml will be of equal sample concentration to a 4-ml concentrate of the Florisil cleanup fraction.

Table 1. Effect of Exposure of Pesticides to Mercury and Copper

| Compound | Percentage Recovery Based on Mean of Duplicate Tests | |
|---|---|---|
| | Mercury | Copper |
| BHC | 81.2 | 98.1 |
| Lindane | 75.7 | 94.8 |
| Heptachlor | 39.8 | 5.4 |
| Aldrin | 95.5 | 93.3 |
| Hept. Epoxide | 69.1 | 96.6 |
| p,p'-DDE | 92.1 | 102.9 |
| Dieldrin | 79.1 | 94.9 |
| Endrin | 90.8 | 89.3 |
| DDT | 79.8 | 85.1 |
| Chlorobenzilate | 7.1 | 0 |
| Aroclor 1254 | 97.1 | 104.3 |
| Malathion, diazinon, Parathion, Ethion, Trithion | 0 | 0 |

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DESCRIPTON OF IMAGERY Potentiometric Surface Map fig 3.2

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DESCRIPTON OF IMAGERY Oil Isopach Map fig 3.3

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DESCRIPTON OF IMAGERY Distribution of PCBS on site fig. 3.5

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DESCRIPTON OF IMAGERY location Map of proposed oil recovery and Monitoring Wells fig. 5-1

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DESCRIPTON OF IMAGERY Survey and Cultural Features of site Fig. 1.2

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DESCRIPTON OF IMAGERY Oil Distribution Map Fig. 3-1

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